NOTES.

1049. *Peroxide-induced Free-radical Addition of Acetamide to Oct-1-ene.*

By Roy J. Gritter and Royce S. Woosley.

Interest in the free-radical addition of small molecules such as acids, esters, anhydrides, etc., to olefins [1] prompts us to report our findings on such additions, and to give the details for one reaction. We have studied many of the same compounds reported in the paper by Allen *et al.*[1] and obtained the same products, but usually in smaller yield. However, a non-rigorous study showed that all the products were partially unsaturated and that unsaturation increased when more peroxide was used. Infrared spectra indicated that the unsaturation was in part αβ-unsaturation; this could be formed by a chain-termination reaction.

The paragraph below describes the addition of acetamide to oct-1-ene in which decanamide was produced in 48% yield, along with indications of a decenamide.

[1] Allen, Cadogan, and Hey, *Chem. and Ind.*, 1962, 1621, and references therein.

Experimental.—Addition of acetamide to oct-1-ene. Acetamide (235·0 g., 4·0 moles) was heated to 150° in a flask equipped with a dropping funnel, a condenser with a mercury-bubbler attached, and a stirrer. A mixture of oct-1-ene (44·8 g., 0·40 mole) and of t-butyl peroxide (8·8 g., 0·06 mole) was added with stirring during 10 hr. and the whole was heated for an additional 2 hr. The mixture was poured into water and heated to 100°. Unchanged acetamide dissolved. The layers were separated and oct-1-ene (2·0 g.) was removed from the top layer to give 46·0 g. of products. Sublimation gave decanamide, m. p. and mixed m. p. 95—97° (lit.,[2] 98°; 20·8 g.), and a residue of higher molecular weight. The infrared spectrum of the amide was that of an authentic sample except for weak bands (6·09, 10·33 μ) indicating unsaturation; [3] the intensity of these bands showed that less than 5% of decenamide could have been produced in the reaction.

This research was supported by the Quartermaster Research and Engineering Center, Natick, Massachusetts.

Department of Chemistry, The University of Connecticut,
Storrs, Connecticut, U.S.A. [*Received, October 8th*, 1962.]

[2] Cheronis and Entriken, " Semimicro Qualitative Organic Analysis," Interscience Publ., Inc., New York, 2nd edn., 1957, p. 552.
[3] Bellamy, " The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, 1954, p. 40.

1050. *The Role of Phenanthraquinone in the Photochemical Oxidation of Ethanol.*

By Peter Walker.

Abstraction of hydrogen from alcohols by photoexcited quinones has been studied in the presence [1,2] and in the absence [3] of oxygen. Quantum efficiencies which approached unity under optimum conditions were observed in all cases and, using steady-state approximations, it was possible to describe reaction mechanisms consistent with the observed data. The present study arose from an investigation of the role of phenanthraquinone in the initiation of photopolymerization.[4]

Table 1.

Quantum efficiency (ϕ) for the disappearance of phenanthraquinone from solutions of ethanol in benzene. (Light intensity $4{\cdot}72 \times 10^{-7}$ einstein min.$^{-1}$.)

[Phenanthraquinone] $\times 10^3$ (mole l.$^{-1}$)	[Ethanol] (mole l.$^{-1}$)	ϕ (average)	[Phenanthraquinone] $\times 10^3$ (mole l.$^{-1}$)	[Ethanol] (mole l.$^{-1}$)	ϕ (average)
1·2	17·10	4·10	4·8	17·10	4·40
	12·83	4·65		8·55	4·35
	8·30	4·20		0·34	2·26
	3·42	3·55		0·18	1·80
	0·68	2·90		0·056	0·90
	0·34	2·30		0·034	0·75
	0·17	1·95			
	0·068	1·95	8·4	2·15	1·60
2·4	12·83	4·95			

In this paper data on quantum efficiency are presented for the photochemical oxidation of ethanol by phenanthraquinone at 4358 Å over a range of ethanol and quinone concentrations (Table 1). At high concentrations of ethanol a quatum efficiency of 4 was attained,

[1] Wells, *Trans. Faraday Soc.*, 1961, **57**, 1703, 1719; *J.*, 1962, 3100.
[2] Bolland and Cooper, *Proc. Roy. Soc.*, 1954, *A*, **225**, 405.
[3] Atkinson and Di, *Trans. Faraday Soc.*, 1958, **54**, 1331.
[4] Notley, U.S.P. 2,951,758/1960.

indicating a chain reaction. The products of the photo-oxidation were acetaldehyde and phenanthrenediol which were formed with quantum efficiencies equal to that with which

TABLE 2.

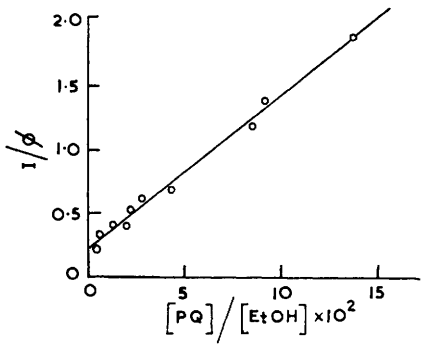
Product yields in the absence of oxygen.

Phenanthraquinone $1{\cdot}2 \times 10^{-3}$M.

[Ethanol] (mole $l.^{-1}$)	[Phenanthrenediol] $\times 10^3$ (mole $l.^{-1}$)	[Acetaldehyde] $\times 10^3$ (mole $l.^{-1}$)
17·10	1·2	1·05
3·42	1·2	1·10
0·17	1·2	1·25

phenanthraquinone (PQ) disappeared from the system (Table 2).* In agreement with the results for the photo-oxidation of ethanol by benzoquinone,[3] only very small amounts of glycol were indicated by periodate tests of the aqueous extracts of irradiated mixtures.

Over the range of conditions studied, a linear relationship was observed between the reciprocal of the quantum efficiency for disappearance of phenanthraquinone and the ratio



Reciprocal quantum efficiency for the disappearance of phenanthraquinone as a function of the ratio [PQ]/[EtOH].

[PQ]/[EtOH] (see Fig.); this indicates a bimolecular deactivation of PQ*. The results for the photo-oxidation of ethanol by phenanthraquinone in the absence of oxygen can be accounted for by the following mechanism (where $[I]$ is the light intensity):

$$PQ + h\nu \longrightarrow PQ^*[I] \quad (1)$$

$$PQ^* + PQ \xrightarrow{k_2} 2PQ \quad (2)$$

$$PQ^* + CH_3{\cdot}CH_2{\cdot}OH \xrightarrow{k_3} PQH{\cdot} + {\cdot}CH(OH){\cdot}CH_3 \quad (3)$$

$$PQH{\cdot} + CH_3{\cdot}CH_2{\cdot}OH \xrightarrow{k_4} PQH_2 + {\cdot}CH(OH){\cdot}CH_3 \quad (4)$$

$${\cdot}CH(OH){\cdot}CH_3 + PQ \xrightarrow{k_5} PQH{\cdot} + CH_3{\cdot}CHO \quad (5)$$

$$2{\cdot}CH(OH){\cdot}CH_3 \xrightarrow{k_6} CH_3{\cdot}CH_2{\cdot}OH + CH_3{\cdot}CHO \quad (6)$$

$$2PQH{\cdot} \xrightarrow{k_7} PQH_2 + PQ \quad (7)$$

The increase of quantum efficiency for the disappearance of phenanthraquinone with increasing concentration of ethanol up to a limiting value, the magnitude of which indicates a chain process, is in qualitative agreement with this mechanism. The yields of acetaldehyde, that of phenanthrenediol, and the amount of phenanthraquinone disappearing were equal as required.

* The decrease in acetaldehyde yield with increasing concentration of ethanol possibly indicates an additional oxidative reaction of PQ*, not considered in this study.

Experimental.—Phenanthraquinone was recrystallized from benzene which had been fractionally distilled from sodium under an atmosphere of nitrogen. The nitrogen (oxygen-free) was purified and presaturated by passage through sintered-disc wash-bottles containing successively Fieser's solution (alkaline dithionite–reduced sodium anthraquinone-2-sulphonate), conc. sulphuric acid, glass wool, and dry benzene. Spectroscopic grade ethanol was used.

Analysis. (*a*) *Phenanthraquinone.* A " Spekker " photometer was used with filters for isolating the 415 mμ band of phenanthraquinone. A calibration curve was prepared for the instrument; control runs using a Cary spectrophotometer confirmed the accuracy of the " Spekker " results within 5%. (*b*) *Phenanthrenediol.* Samples containing phenanthrenediol were passed, in benzene solution, down a column of silver oxide (10 × 1 cm.). The solution was collected and estimated for phenanthraquinone by the previously described method. Control experiments showed that oxidation of phenanthrenediol under these conditions was quantitative. (*c*) *Acetaldehyde.*[5] The benzene solution was extracted with water (4 × 50 ml.), and the combined extracts were diluted to 250 ml; portions of this extract (25 ml.) were estimated for acetaldehyde by the modified Claisen bisulphite method, described by Bolland and Cooper.[2] Control experiments showed that phenanthraquinone and phenanthrenediol did not interfere, consistent results being obtained down to 10^{-3}M acetaldehyde.

Photolysis. An Osram 125w medium-pressure mercury lamp, placed 10 cm. from a quartz lens, gave a roughly parallel beam of light. The mercury line at 4358 Å was isolated by chemical filters,[6] and neutral density filters were used to vary the intensity. The solution to be irradiated was contained in a cell of 3 cm. length with optically-flat ends and a capacity of 40 ml.; a stream of nitrogen having been previously passed into the solution for 30 min.

The light intensity was measured by using the potassium ferrioxalate actinometer.[7] The actinometer solutions and the phenanthraquinone samples absorbed almost completely throughout the irradiations; thus no corrections were applied for unabsorbed radiation. Control runs indicated that the intensity was constant within 10%, which was the general level of accuracy aimed at during these studies.

I thank Dr. W. A. Waters for his interest and encouragement, and acknowledge helpful discussions with my colleagues in the Photo Products Department of E. I. du Pont de Nemours and Co., especially Dr. D. W. Woodward and Dr. A. B. Cohen.

THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY.

[Present address: PHOTO PRODUCTS DEPARTMENT,
E. I. DU PONT DE NEMOURS AND CO.,
PARLIN, NEW JERSEY, U.S.A.]

[*Received, January 12th,* 1963.]

[5] Milton and Waters, " Semimicro Quantitative Analysis," Oxford Univ. Press, 1951, p. 219.
[6] Bowen, " Chemical Aspects of Light," Oxford, 1946.
[7] Hatchard and Parker, *Proc. Roy. Soc.*, 1956, *A*, **235**, 518.

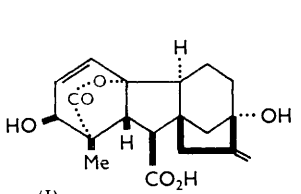
1051. *A Partial Synthesis of* [^{14}C]*Phyllocladene: Some Observations on the Biosynthesis of Gibberellic Acid.*

By A. J. BIRCH and J. WINTER.

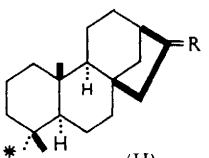
THE probable biosynthetic tetracyclic precursor of gibberellic acid has the skeleton of phyllocladene (II; R = CH_2),[1] and at one stage, when the lactone ring of the former was thought to be β-orientated,[2] phyllocladene itself could have been involved. Accordingly we made [^{14}C]phyllocladene by treating the norketone (II; R = O) with the Wittig reagent from $^{14}CH_3I$. No conversion into gibberellic acid was observed on feeding this phyllocladene to *Gibberella fujikuroi*.

[1] Birch, Rickards, Smith, Harris, and Whalley, *Tetrahedron*, 1959, **7**, 241.
[2] Edwards, Nicolson, Apsimon, and Whalley, *Chem. and Ind.*, 1960, 624.

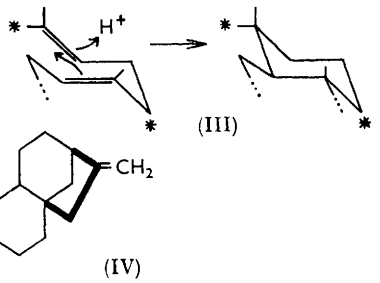
With the establishment [3] of the absolute configuration of gibberellic acid as (I) the earlier tracer results [1] could be used to show that phyllocladene has the wrong configuration [4] to be a precursor. This follows from the fact that the lactone-carbonyl group is unlabelled when the substance is derived from [2-^{14}C]mevalonic lactone, whereas the equatorial α-methyl group of phyllocladene (II), which would require to be oxidised to produce the α-lactone, must carry a full label from the concerted cyclisation of the open-chain precursor shown in (III). The *unlabelled* terminal methyl group (*cis* [5] to the chain) necessarily becomes β and axial, and cannot, after cyclisation, become α and axial, other than by a mechanistically extremely unlikely stereospecific interchange of the two methyl groups. The initial cyclisation must, therefore, involve a mirror-image form of (III). The exact precursor cannot be predicted on this information alone, but it would presumably be enantiomeric at one or both of the centres involving the ring A/B junction. In a personal communication Mr. J. F. Grove and Dr. B. E. Cross (Akers Laboratory, Imperial Chemical Industries Limited) informed us that the authentic precursor is (—)-kaurene [6] (IV) which fulfils these conditions.



(I)



(II)



(III) (IV)

Experimental.—The Wittig reagent [7] was made from methyl iodide ([^{14}C], 2·6 mg., 100 μc, and [^{12}C], 0·05 c.c.) and triphenylphosphine (excess) in benzene, and butyl-lithium (1 equiv.) in tetrahydrofuran (10 c.c.) and 17-norphyllocladan-16-one (II; R = O) (250 mg.) were added. After 8 hr. the mixture was refluxed for 2 hr. and the product worked up, eventually by chromatography on alumina in light petroleum. The initial eluate gave [^{14}C]phyllocladene (52 mg., 30 μc), m. p. 98—99° undepressed on admixture with the authentic substance. This was fed to a culture of *Gibberella fujikuroi* at the Akers Laboratory, in acetone solution, through the kind assistance of Mr. G. S. Nixon and Mr. J. F. Grove. It produced some inhibition of growth; the isolated gibberellic acid (35 mg.) showed no radioactivity.

We are indebted to D.S.I.R. for a scholarship (to J. W.) and to the Rockefeller Foundation for financial assistance. Mr. R. W. Rickards kindly advised in connection with tracer measurements.

Department of Chemistry, University of Manchester. [*Received, March 29th,* 1963.]

[3] Stork and Newman, *J. Amer. Chem. Soc.*, 1959, **81**, 5518; Cross, Grove, McCloskey, Mulholland, and Klyne, *Chem. and Ind.*, 1959, 1345; Masamune, *J. Amer. Chem. Soc.*, 1961, **83**, 1515; McCapra, Scott, Sim, and Young, *Proc. Chem. Soc.*, 1962, 185.

[4] Briggs, Cain, Davis, and Wilmshurt, *Tetrahedron Letters*, 1959, No. 8, 13; Finnegan and Djerassi, *J. Amer. Chem. Soc.*, 1960, **82**, 4342.

[5] Birch, Kocor, Sheppard, and Winter, *J.*, 1962, 1502.

[6] Djerassi, Quitt, Mosettig, Cambie, Rutledge, and Briggs, *J. Amer. Chem. Soc.*, 1961, **83**, 3720. For incorporation, see Cross, Galt, and Hanson, in the press.

[7] Wittig and Scholkopf, *Chem. Ber.*, 1954, **87**, 1318.

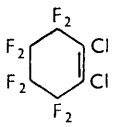
1052. *Antimony Pentafluoride as a Fluorinating Agent.*

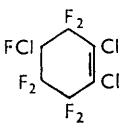
By Karl O. Christe and Attila E. Pavlath.

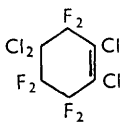
In the reaction of antimony pentafluoride with hexachlorobenzene, which was studied earlier,[1,2] one of the problems was that of controlling the reaction.[2] The use of a general organic solvent to moderate the reaction is impracticable. Most of the compounds which have an acceptable solvent power in relation to the reagent react with antimony pentafluoride. It was found that antimony pentachloride could be used effectively as a solvent for this type of reaction. In most cases no reaction was observed between antimony pentachloride and the organic starting material.

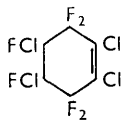
The fluorination of hexachlorobenzene under these conditions resulted in a mixture of thirty-three components, all of which were more volatile than the starting material. The main product, with a yield of 56·1%, was 1,2-dichloro-3,3,4,4,5,5,6,6-octafluorocyclohex-1-ene (I) which has been described by McBee, Wiseman, and Bachman[1] and by Leffler.[2] Leffler obtained and characterised two additional compounds, namely 1,2,4-trichloro-3,3,4,5,5,6,6-heptafluoro- (II) and 1,2,4,4-tetrachloro-3,3,5,5,6,6-hexafluorocyclohex-1-ene (III), in 20% and 5% yield, respectively. Compound (V) has been prepared by Smith *et al.*[3] by the reaction of chloranil with sulphur tetrafluoride.

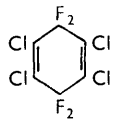
In the present study, five of the thirty-three compounds have been isolated and identified. The first three compounds were identified as (I), (II), and (III). Compounds (IV) and (V) had not been isolated previously in this reaction, and they confirm the reaction mechanism suggested by Leffler.[2]


(I)


(II)


(III)


(IV)


(V)

The structures of the two additional compounds were proved by nuclear magnetic resonance (n.m.r.) spectroscopy and elemental analysis. The n.m.r. spectrum shows, for (V), a singlet at 71·5 p.p.m. (using trichlorofluoromethane as internal standard) which corresponds to one type of fluorine atom. The spectrum of (IV) shows two broad unresolved singlets at 62·5 and 66·7 p.p.m. (using trichlorofluoromethane as internal standard); this indicates two different types of fluorine atom. Since structure (IV) has the highest symmetry of all the theoretically possible structures and is the only one which would result in only two singlets, all the other possibilities can be excluded. The singlet at 66·7 p.p.m. has double the area of that at 62·5 p.p.m. and is therefore assigned to the four fluorine atoms α to the double bond. The singlet at 62·5 p.p.m. is assigned to the two fluorine atoms in the β-positions. No conclusion can be reached, on the basis of n.m.r. spectroscopy, as to the ratio of the three possible isomers (one *trans*- and two *cis*-stereoisomers) obtained, because the two singlets are broad and unresolved. This broadening might be due to the fact that the activation energy required for the transition between the two possible *cis*-stereoisomers is too low for separation of the two individual peaks at room temperature.

An attempt was made to fluorinate tetrachlorophthalic anhydride under similar conditions, but no reaction was observed. Tetrachlorothiophen reacted with a mixture of antimony penta-chloride and -fluoride, but during the reaction desulphurisation occurred,

[1] McBee, Wiseman, and Bachman, *Ind. Eng. Chem.*, 1947, **39**, 415.
[2] Leffler, *J. Org. Chem.*, 1959, **24**, 1132.
[3] Smith, Tullock, Muetterties, Haseck, Fawcett, Engelhardt, and Coffman, *J. Amer. Chem. Soc.*, 1959, **81**, 3165.

the main product being a mixture of *cis*- and *trans*-2,3-dichloro-1,1,1,4,4,4-hexafluorobut-2-ene.

Experimental.—Hexachlorobenzene. Hexachlorobenzene (57 g., 0·2 mole) was dissolved in antimony pentachloride (360 g.) and the mixture refluxed with stirring. Antimony pentafluoride (217 g., 1 mole) was then added slowly and the mixture was heated for an additional 1 hr. The inorganic material was separated by treating the product first with conc. and dil. hydrochloric acid and then with water. The organic part was dissolved in methylene dichloride, dried ($MgSO_4$), and distilled.

There was 48·8% conversion of the starting material and a mixture of thirty-three components was obtained; the five compounds with the highest yields were separated on a preparative gas chromatography column and identified by elemental analysis and n.m.r. spectroscopy. The analytical data are as follows. 1,2-Dichloro-3,3,4,4,5,5,6,6-octafluorocyclohex-1-ene (I) (56·1% yield) (Found: Cl, 24·2. Calc. for $C_6Cl_2F_8$: Cl, 24·05%); 1,2,4-trichloro-3,3,4,5,5,6,6-heptafluorocyclohex-1-ene (II) (5·0% yield) (Found: C, 23·15; Cl, 33·85. Calc. for $C_6Cl_3F_7$: C, 23·1; Cl, 34·1%); 1,2,4,4-tetrachloro-3,3,5,5,6,6-hexafluorocyclohex-1-ene (III) (2·6% yield) (Found: C, 22·4; Cl, 42·95. Calc. for $C_6Cl_4F_6$: C, 22·0; Cl, 43·30%); 1,2,4,5-*tetrachloro*-3,3,4,5,6,6-*hexafluorocyclohex*-1-*ene* (IV) (6·9% yield) (Found: C, 22·25; Cl, 43·15. $C_6Cl_4F_6$ requires C, 22·0; Cl, 43·3%); 1,2,4,5-tetrachloro-3,3,6,6-tetrafluorocyclohexa-1,4-diene (V) (15·7% yield) (Found: C, 24·25; Cl, 49·0. Calc. for $C_6Cl_4F_4$: C, 24·85; Cl, 48·95%).

Tetrachlorophthalic anhydride. Tetrachlorophthalic anhydride (0·33 mole) was dissolved in antimony pentachloride (500 g.) and the mixture refluxed with stirring. Antimony pentafluoride (432 g., 2 moles) was then added slowly and the mixture was heated for an additional 5 hr.; however, no fluorination occurred and only the starting materials could be recovered.

Reaction between tetrachlorothiophen and antimony pentafluoride. Tetrachlorothiophen (111 g., 0·5 mole) was added to antimony pentachloride (500 g.) as solvent. The mixture turned yellow, became hot, and then solidified. Either a solid complex was formed or desulphurisation of the starting material occurred. Antimony pentafluoride (542 g., 2·5 moles) was slowly added, with stirring, to the heated mixture which was then refluxed for 6 hr. The outlet of the condenser was connected to a cold trap (−78°), in which 25 g. of volatile product were collected. An additional 49 g. of product were distilled out of the reaction mixture and combined with the 25 g. from the trap. The product was washed with conc. and dil. hydrochloric acid and water, then dried ($MgSO_4$) and distilled in a spinning-band column. The following fractions were obtained and characterised by their infrared spectra and gas chromatography retention times: 2-chloro-1,1,1,3,4,4,4-heptafluorobut-2-ene (2·0% yield, b. p. 36°); *cis*- and *trans*-2,3-dichloro-1,1,1,4,4,4-hexafluorobut-2-ene (19·5 and 66·0% yields, respectively, b. p. 66—68°); and compounds of higher b. p. (12·5% yield). There was 64% conversion of the starting material. 2-Chloro-1,1,1,3,4,4,4-heptafluorobut-2-ene[4] and *cis*- and *trans*-2,3-dichloro-1,1,1,4,4,4-hexafluorobut-2-ene[5,6] are known compounds.

STAUFFER CHEMICAL COMPANY, RICHMOND RESEARCH CENTER,
RICHMOND 4, CALIFORNIA.

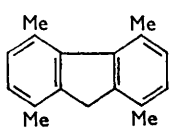
[*Received, April 1st*, 1963.]

[4] Henne and Newby, *J. Amer. Chem. Soc.*, 1948, **70**, 130.
[5] Henne and Trott, *J. Amer. Chem. Soc.*, 1947, **69**, 1820.
[6] Henne, Hinkamp, and Zimmerschied, *J. Amer. Chem. Soc.*, 1945, **67**, 1906.

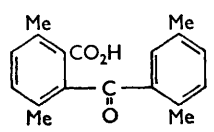
1053. *Constituents of High-boiling Petroleum Distillates. Part VII.*[1] *Synthesis of* 1,4,5,8-*Tetramethylfluorene.*

By W. Carruthers.

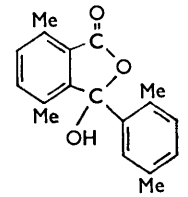
Chromatography of a fraction of a Kuwait mineral oil afforded, among other products, a fluorene derivative, $C_{17}H_{18}$ or $C_{18}H_{20}$.[2] The molecular weight of this hydrocarbon, determined by mass spectroscopy, is 222, corresponding to $C_{17}H_{18}$, and the cracking pattern suggests that the compound is a tetramethylfluorene.[3] This is supported by the infrared spectrum, which shows a single strong maximum in the aromatic C–H out-of-plane deformation region at about 800 cm.$^{-1}$, indicating that each of the benzene rings in the fluorene nucleus has two adjacent hydrogen atoms.[4] A number of structures satisfy these conditions. Most are not easily amenable to synthesis, but the 1,4,5,8-tetramethyl isomer (I) has been obtained conveniently from the tetramethylbenzoylbenzoic acid (II; R = H). Oxidative cyclisation of the acid with potassium persulphate in alkaline



(I)



(II)



(III)

solution, as described by Russell and Thomson,[5] gave 1,4,5,8-tetramethylfluorenone in poor yield, whence reduction with hydrogen iodide in propionic acid [6] led to the hydrocarbon (I). It was not identical with the compound from the oil.

The tetramethylbenzoylbenzoic acid was best prepared from 3,6-dimethylphthalic anhydride and *p*-xylylmagnesium bromide. Friedel–Crafts condensation of the anhydride and *p*-xylene afforded a less pure product (cf. Newman and Lord [7]). The acid appears to exist largely in the cyclic " pseudo "-form (III) for the infrared spectrum (in Nujol) has strong hydroxyl absorption at 3500 cm.$^{-1}$ and a single carbonyl maximum at 1740 cm.$^{-1}$ (cf. Graf *et al.*[8]). The ultraviolet spectrum is similar to that of typical " pseudo "-esters and does not show the maximum at about 250 mμ characteristic of the " normal " form of *o*-benzoylbenzoic acids.[8,9] The methyl ester, prepared with diazomethane, has the " normal " structure (II; R = Me), as expected.[9]

Experimental.—M. p.s were determined on a Kofler block. Ultraviolet spectra were recorded with a Unicam S.P. 700 spectrophotometer and refer to solutions in 95% ethanol unless stated otherwise; values in parentheses refer to shoulders. Infrared spectra were obtained with a Perkin-Elmer Infracord instrument.

3,6-*Dimethyl*-2-(2,5-*dimethylbenzoyl*)*benzoic acid.* A solution of *p*-xylylmagnesium bromide, prepared from bromo-*p*-xylene (12·7 g.) and magnesium (1·7 g.), in ether (150 ml.) was added dropwise to a stirred solution of 3,6-dimethylphthalic anhydride (13·3 g.) in benzene (200 ml.). Ether was distilled off and the stirred mixture was heated at 60° for 4 hr. The cooled mixture was decomposed with ice and hydrochloric acid, and the benzene layer was separated and extracted with sodium carbonate. Acidification with acetic acid gave the *acid* (8·1 g.). It

[1] Part VI, *Nature*, 1961, **192**, 256.
[2] Carruthers and Douglas, *J.*, 1957, 278.
[3] Personal communication from Mr. W. L. Mead, British Petroleum Company, Limited.
[4] Bellamy, " The Infra-red Spectra of Complex Molecules," Second edn., Methuen and Co., Ltd., London, 1958, p. 75.
[5] Russell and Thomson, *J.*, 1962, 3379.
[6] Morrison, *J. Org. Chem.*, 1958, **23**, 1772.
[7] Newman and Lord, *J. Amer. Chem. Soc.*, 1944, **66**, 733.
[8] Graf, Girod, Schmid, and Stoll, *Helv. Chim. Acta*, 1959, **42**, 1085.
[9] Newman and Muth, *J. Amer. Chem. Soc.*, 1951, **73**, 4627.

formed prisms (from cyclohexane–benzene) which melted at 150—152°, partly resolidified, and melted again at 171—173° (Found: C, 76·7; H, 6·5. $C_{18}H_{18}O_3$ requires C, 76·6; H, 6·4%), $\lambda_{max.}$ (in cyclohexane) (236), 278, 282, and 292 mμ [log ε (4·02), 3·39, 3·40, and 3·41]. The *methyl ester*, prepared from the acid and ethereal diazomethane, had b. p. 180° (bath)/0·5 mm. (Found: C, 77·05; H, 6·9. $C_{19}H_{20}O_3$ requires C, 77·0; H, 6·8%), $\lambda_{max.}$ 253 and 294 mμ (log ε 3·97 and 3·46), $\nu_{max.}$ 1740 and 1670 cm.$^{-1}$.

1,4,5,8-*Tetramethylfluorenone*. A solution of potassium persulphate (3·9 g.) in water (30 ml.) was added all at once to a hot (boiling-water bath) stirred solution of the above acid (3·9 g.) in 2N-sodium hydroxide (20 ml.) and water (80 ml.). The solution was stirred at 95° for 3 hr., and small amounts of sodium hydroxide solution were added from time to time to keep the reaction alkaline. The cooled alkaline solution was extracted with ether, and the recovered neutral gum (380 mg.) was chromatographed on alumina. Elution with light petroleum (b. p. 60—80°)–benzene (4 : 1) gave the *fluorenone* (150 mg.) as yellow needles, m. p. 108—109° (from methanol) (Found: C, 86·75; H, 6·7. $C_{17}H_{16}O$ requires C, 86·4; H, 6·8%), $\lambda_{max.}$ 255, 262, 318, 332, 342, and 380—385 mμ (log ε 4·61, 4·69, 3·53, 3·57, 3·56, and 3·10), $\nu_{max.}$ (KBr disc) 1690 cm.$^{-1}$.

1,4,5,8-*Tetramethylfluorene*. A solution of the above fluorenone (140 mg.) and hydriodic acid (*d* 1·94; 2 ml.) in propionic acid (12 ml.) was boiled with red phosphorus (150 mg.) for 60 hr. The cooled mixture was extracted with ether and benzene, and the extract was washed with sodium hydroxide solution and water. The neutral brown gum was chromatographed on alumina; elution with light petroleum (b. p. 60—80°)–benzene (4 : 1) gave the *fluorene* (120 mg.) as blades, m. p. 122—124° (from ethanol–benzene) (Found: C, 92·0; H, 8·0. $C_{17}H_{18}$ requires C, 91·8; H, 8·2%), $\lambda_{max.}$ (265), 270, and (296) mμ [log ε (4·43), 4·44, and (3·58)], $\nu_{max.}$ (KBr disc) 802 cm.$^{-1}$.

I thank Sir James Cook, F.R.S., for his interest.

MEDICAL RESEARCH COUNCIL UNIT, WASHINGTON SINGER LABORATORIES,
THE UNIVERSITY, EXETER. [*Received, April 4th*, 1963.]

1054. *Synthesis of Various Peptides containing* L-*Arginine,* L-*Alanine, and* D-*Alanine.*

By G. HARRIS and I. C. MACWILLIAM.

PEPTIDES containing arginine were required for testing as nutrients for arginine-deficient mutants of *Saccharomyces cerevisiae*. Such peptides, particularly tetrapeptides, were also desired for assimilation experiments with a wider range of yeasts. L-Arginyl-L-alanyl-L-arginyl-L-alanine and its dipeptide precursor were already available.[1] The present Note describes the preparation of the corresponding peptides containing D-alanine in place of L-alanine residues, and of those having L-alanyl-L-arginine in place of the L-arginyl-L-alanine units. The results of the assimilation tests are described elsewhere.[2]

Experimental.—(*a*) N^{ϵ}-Nitro-L-arginine (20 g.) was treated [3] with benzyl alcohol (50 ml.) and polyphosphoric acid (50 g.). N^{ϵ}-*Nitro-L-arginine benzyl ester* crystallised as needles (70%) from methanol–ether and had m. p. 171—173°, $[\alpha]_D^{20}$ +15° in MeOH (Found: C, 53·2; H, 6·5; Cl, 10·4; N, 20·4. $C_{13}H_{22}ClN_5O_2$ requires C, 53·3; H, 6·4; Cl, 10·4; N, 20·5%).

(*b*) *N*-Benzyloxycarbonyl-L-alanine [10 g.; m. p. 81—82° (lit.,[4] 84°)] in tetrahydropyran (30 ml.) was shaken with N^{ϵ}-nitro-L-arginine benzyl ester (16 g.) in the same solvent after addition of dicyclohexylcarbodi-imide (5 g.). N-*Benzyloxycarbonyl-L-alanyl-*N^{ϵ}*-nitro-L-arginine benzyl ester* was isolated [1] and crystallised (22 g., 85%) from aqueous ethanol as plates, m. p.

[1] Harris and MacWilliam, *J.*, 1961, 2053.
[2] Harris, MacWilliam, and Merritt, to be published.
[3] Erlanger and Hall, *J. Amer. Chem. Soc.*, 1954, **76**, 5781.
[4] Werbin and MacLaren, *J. Amer. Chem. Soc.*, 1951, **73**, 501.

150—151°, $[\alpha]_D^{22}$ −13·3° in MeOH (Found: C, 55·8; H, 6·0; N, 16·4. $C_{24}H_{30}N_6O_7$ requires C, 56·0; H, 5·8; N, 16·3%).

(*c*) The benzyl ester above (5 g.) was saponified as described earlier.[1] *N*-Benzyloxycarbonyl-L-alanyl-*N*$^{\epsilon}$-nitro-L-arginine (3·7 g., 85%) crystallised from aqueous ethanol and had m. p. 172—173°, $[\alpha]_D^{22}$ −10° in MeOH (lit.,[5] m. p. 171—172°, $[\alpha]_D^{25}$ −9·4° in MeOH) (Found: N, 19·9. Calc. for $C_{17}H_{24}N_6O_7$: N, 20·1%).

(*d*) The preceding derivative (2 g.) was hydrogenated.[1] Evaporation of the solvent yielded L-alanyl-L-arginine which, recrystallised from aqueous ethanol, had m. p. 165—166°, $[\alpha]_D^{22}$ +9° in H_2O (0·9 g., 75%) (Found: N, 22·8. Calc. for $C_{11}H_{22}N_5O_5$: N, 22·9%). Hofmann *et al.*[5] found m. p. 166—168°, $[\alpha]_D^{27}$ +8·7° in H_2O.

(*e*) Benzyloxycarbonyl-L-alanyl-*N*$^{\epsilon}$-nitro-L-arginine benzyl ester (5 g.) in carbon tetrachloride (100 ml.) was treated with dry hydrogen chloride.[1] *L-Alanyl-N*$^{\epsilon}$*-nitro-L-arginine benzyl ester* (3·1 g., 77%) was produced and recrystallised from methanol–ether as needles, m. p. 141°, $[\alpha]_D^{22}$ −11° in MeOH (Found: C, 46·4; H, 5·7; N, 20·0. $C_{16}H_{25}ClN_6O_5$ requires C, 46·2; H, 5·8; N, 20·2%).

(*f*) *N*-Benzyloxycarbonyl-L-alanyl-*N*$^{\epsilon}$-nitro-L-arginine (2·2 g.) was condensed with the preceding ester (2·0 g.) as described earlier.[1] *N-Benzyloxycarbonyl-L-alanyl-N*$^{\epsilon}$*-nitro-L-arginyl-L-alanyl-N*$^{\epsilon}$*-nitro-L-arginine benzyl ester* separated from aqueous ethanol as plates (3·0 g., 73%), m. p. 196—197°, $[\alpha]_D^{22}$ −7·3° in MeOH (Found: C, 50·6; H, 5·6; N, 21·0. $C_{33}H_{46}N_{12}O_{11}$ requires C, 50·4; H, 5·9; N, 21·4%).

(*g*) The last-mentioned product (2 g.) was hydrogenated [1] and yielded *L-alanyl-L-arginyl-L-alanyl-L-arginine*. This crystallised as the diacetate from aqueous ethanol in the form of plates (0·9 g., 55%), m. p. 246° (decomp.), $[\alpha]_D^{22}$ +8·2° in H_2O (Found: C, 44·9; H, 7·4; N, 23·9. $C_{18}H_{36}N_{10}O_5,2CH_3{\cdot}CO_2H$ requires C, 44·6; H, 7·5; N, 23·7%).

The *compounds* listed in the Table were prepared by methods analogous to those described [1] for the L-arginyl-L-alanyl analogues.

Properties and analyses of D-alanine derivatives.

No.	Peptide	Starting material (g.)	Yield (g.)
1	D-Alanine benzyl ester	5	9·7
2	*N*α-Benzyloxycarbonyl-*N*$^{\epsilon}$-nitro-L-arginyl-D-alanine benzyl ester	arg, 11, +ester, 9	12·1
3	*N*α-Benzyloxycarbonyl-*N*$^{\epsilon}$-nitro-L-arginyl-D-alanine	4	2·8
4	L-Arginyl-D-alanine	2	1·0
5	*N*$^{\epsilon}$-Nitro-L-arginyl-D-alanine benzyl ester	2	1·4
6	*N*α-Benzyloxycarbonyl-*N*$^{\epsilon}$-nitro-L-arginyl-D-alanyl-*N*$^{\epsilon}$-nitro-L-arginyl-D-alanine benzyl ester	1·0+ ester, 1·2	1·3
7	L-Arginyl-D-alanyl-L-arginyl-D-alanine	1·0	0·5

				Found (%)				Required (%)		
No.	Form	M. p.	[α]	C	H	N	Formula	C	H	N
1	Needles *	139°	$[\alpha]_D^{22}$ +13° in H_2O	55·6	6·7	6·5	$C_{10}H_{14}ClN_2O_4$	55·8	6·5	6·5
2	Plates	143—144	$[\alpha]_D^{20}$ −3° in MeOH	56·1	6·0	16·2	$C_{24}H_{30}N_6O_7$	56·0	5·8	16·3
3	Needles	184—185	$[\alpha]_D^{23}$ +4° in pyridine	47·9	5·8	20·0	$C_{17}H_{24}N_6O_7$	48·1	5·7	19·8
4	,,	151—152	$[\alpha]_D^{23}$ +16° in H_2O	43·0	7·8	22·7	$C_{11}H_{23}N_5O_6$	43·3	7·6	22·9
5	,,	156—157	$[\alpha]_D^{23}$ −3° in MeOH	46·0	5·5	20·4	$C_{16}H_{25}ClN_6O_5$	46·2	5·8	20·2
6	Plates	197	$[\alpha]_D^{22}$ +4·4° in MeOH	50·6	6·0	21·7	$C_{33}H_{46}N_{12}O_{11}$	50·4	5·9	21·4
7	Amorphous	—	$[\alpha]_D^{23}$ +15° in H_2O	44·8	7·3	23·9	$C_{18}H_{36}N_{10}O_5,2CH_3{\cdot}CO_2H$	45·1	7·5	24·1

* Hydrochloride.

BREWING INDUSTRY RESEARCH FOUNDATION,
NUTFIELD, SURREY.

[*Received, April 9th,* 1963.]

[5] Hofmann, Peckham, and Rheiner, *J. Amer. Chem. Soc.*, 1956, **78**, 238.

1055. *The Nitration of Fluoroxylenes and Subsequent Reactions.*

By G. VALKANAS.

IN a study of the preparation of highly fluorinated aromatic hydrocarbons we attempted the nitration of fluoroxylenes, using the conditions that Schiemann employed for fluorotoluenes.[1] The exceedingly exothermic reaction was not easily controlled. Addition of fuming nitric acid to fluoroxylenes with external cooling,[1] led to uncontrolled reaction. Slow addition of fuming nitric acid at −15° to −30° (internal cooling with solid carbon dioxide) led to well-controlled mononitration. The isomeric fluoroxylenes had different reactivities, and in some cases heating was necessary to complete the reaction.

Isolation of the nitration products of fluorotoluenes by fractionation permitted effective separation.[1] The number of mononitrated isomeric products is lower for fluoroxylenes and the differences in b. p. are greater. High proportions of *p*-fluoronitroxylenes are expected [2] and this was used to distinguish the fractions. Distillation cuts having a b. p. difference of less than 1·0° at 14 mm., when obtained in yields higher than 50% of product, were taken as *p*-fluoronitroxylenes; these, before further use, were fractionated 2—3 times more and then appeared to be >98% pure on gas chromatography on two different columns.

The structures of the mononitration products are based on two assumptions, namely, that (*a*) if one compound is produced the nitro-group is placed *para* to the fluorine atom, and (*b*) if two isomers are isolated the one of lower b. p. has the nitro-group *para* to fluorine,[3] this being also the compound produced in greater amount. Thus fluoro-*p*-xylene is taken to give 2-fluoro-5-nitro-1,4-xylene, and 3-fluoro-1,2-xylene is assumed to give 3-fluoro-6-nitro-1,2-xylene for lower-boiling distillate. 2- and 5-Fluoro-1,3-xylene each gave the two possible mononitration compounds, the structures of which are assigned on the above principles. Various fluoronitroxylenes have also been prepared from nitroxylidines by Wittig and Härle.[3]

4-Fluoro-1,2-xylene could not be nitrated. At −30° to −40° the experiment gave only polynitroxylenols. This parallels the nitration of *p*-fluorotoluene [1] and the unusually large reactivity of *o*-nitro-substituted fluorinated aromatic hydrocarbons.[4] It seems that the reactivity of fluorine *ortho* to a nitro-group is further increased by a *p*-methyl-fluorine relation.

The fluoronitroxylenes were easily reduced to fluoroxylidines, either by stannous chloride in hydrochloric acid [5] or by iron in boiling 0·05—0·1N-ammonium chloride.[6] The fluoroxylidines were sensitive to light, so they were characterised and analysed as picrates. They afforded difluoroxylenes by the fluoroborate process.[7] The latter are light liquids of characteristic smell, their boiling points being close to each other and to those of fluorine-free xylenes and monofluoroxylenes.

The fluoroxylenes were prepared satisfactorily from the corresponding xylidines by the Schiemann reaction. Two of the six possible isomers, 4-fluoro-1,3-xylene [1] and fluoro-1,4-xylene,[8] were already known, the second having been prepared by diazotisation in anhydrous hydrogen fluoride.

Experimental.—*4-Fluoro-1,2-xylene.* 3,4-Xylidine (60 g.) was diazotised in concentrated hydrochloric acid (200 ml.) by sodium nitrite (35 g.) in water (50 ml.) at −5° to 0°. Addition

[1] Schiemann, *Ber.*, 1929, **62**, 1794.
[2] de la Mare and Ridd, " Aromatic Substitution. Nitration and Halogenation," Academic Press, Inc., New York, 1959, p. 85.
[3] Wittig and Härle, *Annalen*, 1959, **623**, 17.
[4] Bergmann, Blum, Butanaro, and Heller, *Tetrahedron Letters*, 1959, No. 1, 15.
[5] Finger, Reed, and Finnerty, *J. Amer. Chem. Soc.*, 1951, **73**, 153.
[6] Valkanas and Hopff, *J.*, 1963, 1925; Finger and Reed, *J. Amer. Chem. Soc.*, 1944, **66**, 1972.
[7] Roe, *Org. Reactions*, 1949, **5**, 193.
[8] Fern and Wanderwerf, *J. Amer. Chem. Soc.*, 1950, **72**, 4809.

of 40% fluoroboric acid (110 ml.) gave a heavy precipitate which was filtered off, washed successively with a little cold water, cold 1 : 1 v/v methanol–ether, and ether, and dried (yield, 93 g., 90%; decomp. 84—85°). The diazonium salt was dried for 3 hr. *in vacuo* at room temperature and then thermally decomposed.[7] (This and the other xylenediazonium fluoroborates decompose in *ca.* 10 hr. at room temperature.) The decomposition product was steam-distilled and the distillate extracted with ether. Fractional distillation gave 4-*fluoro*-1,2-*xylene*, b. p. 143—144°/730 mm. (47·8 g., 77%) (Found: F, 15·25. C_8H_9F requires 15·3%).

Other monofluoroxylenes. These were prepared similarly. The xylidines used had a claimed purity of at least 98% (" Fluka "-Switzerland, puriss.) and their identities were confirmed by preparing derivatives reported in the literature.[9]

Nitration of 3-*fluoro*-1,2-*xylene.* 3-Fluoro-1,2-xylene (30 g.) was cooled to −10° and nitric acid (30 ml.; *d* 1·51) was added to it during 1 hr., with stirring, while the temperature was kept below −15° by internal cooling with solid carbon dioxide. The mixture was stirred at −15°

Compounds prepared.

Benzenediazonium fluoroborates.	Yield (%) *	Decomp.		Yield (%) *	Decomp.
2,3-Dimethyl-	86	57—58°	3,5-Dimethyl-	76	77—78°
3,4-Dimethyl-	90	84—85	4-Fluoro-2,5-dimethyl-	36	63—64
2,5-Dimethyl-	75	70—72	4-Fluoro-3,5-dimethyl-	38	62—64
2,6-Dimethyl-	76	74—75	4-Fluoro-2,3-dimethyl-	41	70—72

			Found (%)		
Fluoroxylenes.	Yield (%) *	B. p./730 mm.	C	H	F
3-Fluoro-1,2-xylene †	53	142—143°	77·2	7·1	15·1
4-Fluoro-1,2-xylene †	77	143—144	—	—	15·25
2-Fluoro-1,4-xylene †	49	137—138	77·3	7·3	15·1
5-Fluoro-1,3-xylene †	62	138—139	—	—	15·2
2,5-Difluoro-1,3-xylene ‡	25	142—143	68·1	5·5	26·65
2,5-Difluoro-1,4-xylene ‡	27	141—142	68·0	5·4	26·5
3,6-Difluoro-1,2-xylene ‡	30	137—138	68·1	5·6	26·4

			Picrates ¶			
Fluoroxylidines (NH_2 = 1).	B. p./14 mm.	Yield (%) §	M. p.	C (%)	H (%)	F (%)	N (%)
4-Fluoro-3,5-dimethylaniline	93—94°	84	195—196°	47·8	3·0	5·4	15·9
4-Fluoro-2,6-dimethylaniline	91—92	78	207—208	47·6	3·1	5·5	16·2
4-Fluoro-2,5-dimethylaniline	98—99	69	190—191	—	—	5·5	16·1
4-Fluoro-2,3-dimethylaniline	101—102	89	207—208	—	—	5·6	15·9

* Calc. on the amine. † C_8H_9F requires C, 77·5; H, 7·2; F, 15·3%. ‡ $C_8H_8F_2$ requires C, 68·0; H, 5·5; F, 26·4%. § Calc. on nitro-compound. ¶ $C_{14}H_{11}FN_4O_6$ requires C, 48·0; H, 3·15; F, 5·45; N, 16·0%.

for a further ½ hr., then allowed slowly to reach room temperature. To complete the nitration the mixture was heated at 40—50° for 1 hr.; evolution of nitric oxides occurred and the solution became brown. It was poured on ice. A yellow precipitate (38 g.) separated. By fractionation under reduced pressure through a 60 cm. column, two main fractions were collected: (1) b. p. 109—110°/14 mm., m. p. 36—37° (from methanol) (23·2 g., 61%), 1-*fluoro*-2,3-*dimethyl*-4-*nitrobenzene* (Found: F, 11·3; N, 8·45. $C_8H_8FNO_2$ requires F, 11·2; N, 8·4%); and (2) b. p. 112—130°/14 mm. (12·4 g.).

Nitration of 2-, 4- *and* 5-*fluoro*-1,3-*xylene.* (*a*) 2-Fluoro-1,3-xylene (30 g.) was treated with nitric acid (30 ml.; *d* 1·51) as described above. The mixture was stirred at −15° for a further hour, then allowed slowly to reach room temperature. To complete nitration, heating at 40—50° for 1 hr. was necessary. Pouring the mixture on ice gave a yellow precipitate that, when fractionated, afforded fractions (1) b. p. 107—108°/14 mm., m. p. −1° (20 g., 49·5%), 2-*fluoro*-1,3-*dimethyl*-4-*nitrobenzene* (Found: F, 11·35; N, 8·4%), and (2) b. p. 111—112°/14 mm., m. p. 42—43° (from methanol) (18 g., 44%), 2-*fluoro*-1,3-*dimethyl*-5-*nitrobenzene* (Found: F, 11·4%).

(*b*) 4-Fluoro-1,3-xylene [1] gave 85% of mononitration product when treated as described

[9] Yokoyama, *Helv. Chim. Acta*, 1929, **12**, 771; Stephen, Short, and Gladding, *J.*, 1920, **117**, 526; Haller, Adams, and Wherry, *J. Amer. Chem. Soc.*, 1920, **42**, 1842.

above, and 6—7% of nitroxylenols. Heating of the reaction mixture should be avoided. Storage at room temperature ensured complete nitration. Fractionation gave only one product, b. p. 103—105°/14 mm. Evidently, the two isomers expected are of similar b. p. and separation by fractionation was unsuccessful.

(*c*) In the nitration of 5-fluoro-1,3-xylene (30 g.) more care is needed to control the reaction. The nitration mixture was allowed carefully to reach room temperature and then kept for 3 hr. with stirring. Fractionation afforded two fractions (1) b. p. 93—94°/14 mm., m. p. 51—52° (from methanol) (24·5 g., 60%), *5-fluoro-1,3-dimethyl-2-nitrobenzene* (Found: F, 11·5; N, 8·3%), and (2) b. p. 102—103°/14 mm., m. p. 50—51° (from methanol) (13·5 g., 33%), *1-fluoro-3,5-dimethyl-2-nitrobenzene* (Found: F, 11·4%).

Nitration of fluoro-1,4-xylene. To fluoro-*p*-xylene (30 g.), nitric acid (30 ml.; *d* 1·51) was added during 1½ hr. with stirring, the temperature being kept at −15° by internal cooling as above. The solution was kept at −15° for a further ½ hr., then allowed to reach room temperature and heated for 2 hr. at 40—50° A yellow precipitate resulted when the solution was poured on ice. It was extracted with ether, dried, and fractionated, giving fractions (1) b. p. 95—96°/14 mm., m. p. 32—33° (3·7 g., 9%), and (2) b. p. 107—107·5°/14 mm., m. p. 49—50° (31·4 g., 77%), *2-fluoro-1,4-dimethyl-5-nitrobenzene* (Found: F, 11·4%).

4-Fluoro-2,3-dimethylaniline. This was obtained by boiling the corresponding nitro-compound (30 g.) in 0·05N-ammonium chloride (500 ml.) containing an excess of iron turnings (100 g.).[6] After 6 hours' refluxing the amine was obtained by steam-distillation. After extraction with ether and fractionation it had b. p. 101—102°/14 mm. (18·7 g., 76%), m. p. 39—40°. Reduction with stannous chloride in concentrated hydrochloric acid [5] for 4 hr. on the water-bath gave the amine in higher yield (89%). The amine (0·5 g.) with picric acid (1·5 g.) in hot ethanol (50 ml.) gave, after cooling, the *picrate* which, recrystallised from methanol, had m. p. 207—208° (Found: F, 5·6; N, 15·9. $C_{14}H_{11}FN_4O_8$ requires F, 5·45; N, 16·0%).

The other *fluoroxylidines* reported in the Table were prepared by use of ammonium chloride and iron.

2,5-Difluoro-1,3-xylene. 4-Fluoro-2,6-dimethylaniline (15 g.) was added to 40% fluoroboric acid solution (60 ml.). Sodium nitrite (7·6 g.) in water (15 ml.) was added dropwise to it at −5° to 0°. The resulting precipitate was filtered off, washed successively with a little cold water, 1 : 1 v/v methanol–ether, and ether. It was dried for 1 hr. *in vacuo* (10·9 g., 42%; decomp. 62—64°) and thermally decomposed.[7] The decomposition residue was steam-distilled and the distillate extracted with ether. The *difluoroxylene* had b. p. 142—143°/730 mm. (3·8 g., 25%) (Found: C, 68·1; H, 5·5; F, 26·65. $C_8H_8F_2$ requires C, 68·0; H, 3·15; F, 26·4%).

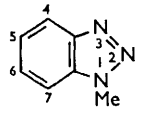
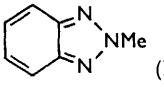
The other *difluoroxylenes* reported in the Table were prepared in the same way.

LABORATORY OF ORGANIC CHEMICAL TECHNOLOGY,
SWISS FEDERAL INSTITUTE OF TECHNOLOGY, ZURICH. [*Received, April 9th*, 1963.]

1056. *Nuclear Magnetic Resonance and Ultraviolet Spectra of Benzotriazole and its 1- and 2-Methyl Derivatives.*

By N. K. ROBERTS.

BENZOTRIAZOLE gives, on methylation, its 1- (I) and 2-methyl derivative (II). The ultraviolet (u.v.) absorption spectra of benzotriazole and its 1-methyl derivative are very

(I)  (II) 

similar to one another (see Table) and different from that of the 2-methyl derivative. The similarity has been interpreted [1] as due to dominance of the molecular state of benzotriazole by the asymmetric tautomeric group NH·N:N.

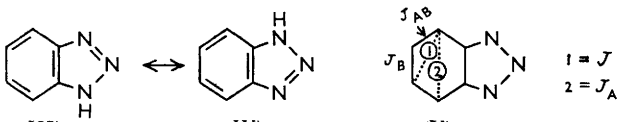
[1] Casoni, Mangini, Passerini, and Zauli, *Gazzetta*, 1958, **88**, 977.

Ultraviolet absorption spectra ($\lambda_{max.}$ in Å; $10^{-3}\varepsilon$ in parentheses).

Benzotriazole		2535 (6·35)	2589 (6·29)		2750 (5·32)	
1-Me deriv.		2564 (6·78)	2620 (6·82)		2792 (5·10)	
2-Me deriv.	2169 (18·4)	2512 (5·64)		2791 (1·49)	2844 (1·70)	2941 (1·38)

On the other hand, the proton nuclear magnetic resonance (n.m.r.) spectra (operating frequency 29·9200 Mc./sec.) of benzotriazole and its 2-methyl derivative are very similar, the only obvious difference being the peak due to the methyl group. The spectrum of the protons in the 6-membered ring is typical for an A_2B_2 system, as in naphthalene. The proton attached to the nitrogen in the parent molecule is not observed, probably owing to the exchange process mentioned below rather than to the quadrupole relaxation of the nitrogen nucleus. The spectrum due to the ring-protons in 1-methylbenzotriazole is quite different from that in the parent or the 2-methyl derivative, the only similarity being the methyl peak in approximately the same position for the two derivatives.

The u.v. and n.m.r. spectra can be reconciled if the proton attached to nitrogen in the parent undergoes rapid exchange between equivalent positions (III) $\rightleftharpoons$ (IV). If the rate



(III) (IV) (V)

of exchange is greater than the coupling constants between this proton and the ring-protons, and if there is no coupling between the adjacent nitrogen nuclei and the ring-protons, then the spectrum of these protons will appear as an A_2B_2 spectrum, of the type shown by naphthalene. It is known that the nitrogen nucleus couples very weakly with protons in adjacent alkyl groups.[2]

The coupling constants for benzotriazole and its 1-methyl derivative were determined by analysing the spectra on the basis of an A_2B_2 system with $J_A = 0$ (cf. V).[3] The side-band technique was used for measuring line separations and the results are tabulated here, together with those for naphthalene.[3] As a check on the analysis the calculated and the experimental line positions were compared: differences nowhere exceeded 0·1 c./sec. ($\nu_0\delta$ is the chemical shift). It is not possible from the spectra to decide whether the protons situated at position 4 and 7 or 5 and 6 are up-field. (This could be ascertained from the spectra of, *e.g.*, 5-deuteriobenzotriazole. Measurements for 2-deuterionaphthalene [3] showed that the protons at positions 5 and 6 were up-field. The hetero-ring would be expected to enhance this behaviour.)

N.m.r. coupling constants (J in c./sec.).

Compound	Solvent	J_B	J_{AB}	J	$\nu_0\delta$
Benzotriazole	Acetone	6·7	8·3	1·4	13·3
2-Methylbenzotriazole	—	3·6	9·4	0·5	19·9
Naphthalene	Dioxan	6·0	8·6	1·4	14·3

The similarity of the coupling constants for naphthalene and benzotriazole suggests that the ring of protons in the latter is aromatic, in agreement with the structure indicated by the u.v. spectrum of benzotriazole and its 1-methyl derivative.[1] The greater value of J_{AB} and the smaller value of J_B for compound (II) suggest the quinone-type structure for the ring, the localised double bands being expected to cause such changes.

[2] Jackman, " Nuclear Magnetic Resonance," Pergamon Press, London, 1959, p. 56.
[3] Pople, Schneider, and Bernstein, *Canad. J. Chem.*, 1957, **35**, 1060.

Finally, it is clear from the n.m.r. spectrum of the 1-methyl derivative that strong coupling takes place between the ring-protons and the methyl group on the adjacent nitrogen atom.

I wish to thank Dr. R. E. Richards of Lincoln College, Oxford, for the use of his high-resolution n.m.r. spectrometer [4] and the hospitality of his laboratory, also Dr. C. Taylor of the Biochemistry Department who supplied pure samples of the compounds.

PHYSICAL CHEMISTRY LABORATORY, THE UNIVERSITY, OXFORD.
[Present address: CHEMISTRY DEPARTMENT, UNIVERSITY OF TASMANIA, HOBART, TASMANIA.] [*Received, March 25th*, 1963.]

[4] Leane, Richards, and Schaefer, *J. Sci. Instr.*, 1959, **36**, 230.

1057. *The Reaction of Isocyanates with Phosphorus Pentachloride.*

By HENRI ULRICH and A. A. R. SAYIGH.

ALTHOUGH phosphorus pentachloride usually converts carbonyl compounds into the gem.-dichlorides, Gumpert [1] was unable to isolate *N*-dichloromethyleneaniline from the intractable mixture which he obtained on treatment of phenyl isocyanate with phosphorus pentachloride. We have found that *o*-tolyl isocyanate (I) does not react with phosphorus pentachloride at room temperature, but that at 100° a vigorous reaction ensues with evolution of carbonyl chloride. Attempted distillation then led to extensive decomposition, but it was possible to isolate 10% of *N*-dichloromethylene-*o*-toluidine (II). This was identified by comparison with a sample prepared by chlorination of the formimidoyl chloride obtained by reaction of *N*-*o*-tolylformamide and carbonyl chloride.[2]

Refluxing the crude 100° reaction mixture in *o*-dichlorobenzene (180°) caused a further reaction, as shown by changes in the infrared spectrum. A strong absorption at 4·7 μ developed, due to the formation of di-*o*-tolylcarbodi-imide (III), which was subsequently isolated.

Infrared examination also indicated the presence of phosphorus oxychloride in the mixture after the initial reaction. It has been reported [3] that this compound catalyses the formation of carbodi-imides from aryl isocyanates. That such an effect was not in operation in this case was proved by showing that no reaction took place between the phosphorus oxychloride and *o*-tolyl isocyanate or *N*-dichloromethylene-*o*-toluidine. Nor

$$\underset{\text{(I)}}{R\cdot NCO} + PCl_5 \longrightarrow \underset{\text{(II)}}{R\cdot N{:}CCl_2} + POCl_3 + \underset{\text{(III)}}{R\cdot N{:}C{:}N\cdot R} + COCl_2$$

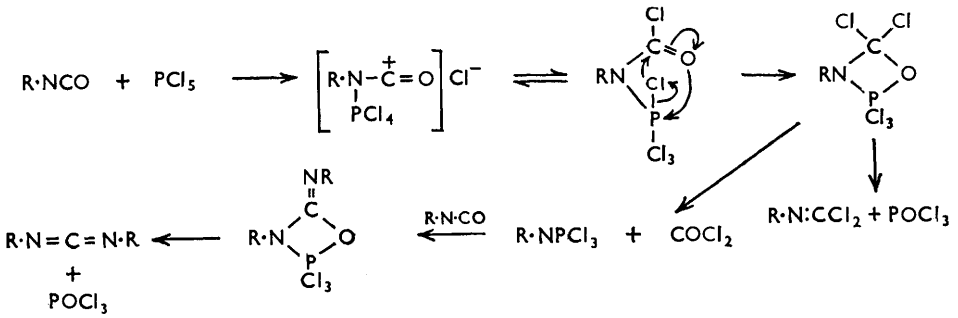
$$\underset{\text{(IV)}}{R\cdot NPCl_3} \longrightarrow \underset{\text{(V)}}{\begin{matrix} R\cdot N-PCl_3 \\ | \quad | \\ R\cdot N{:}C-O \end{matrix}} \qquad (R = o\text{-tolyl})$$

did *o*-tolyl isocyanate and *N*-dichloromethylene-*o*-toluine direact with each other. So, to account for the formation of the carbodi-imide, we suggest that *o*-tolyl trichlorophosphazene (IV) is its precursor. Dimeric trichlorophosphazenes dissociate to the monomers above 150° and then react with isocyanates to yield carbodi-imides.[4] Since in the present case, isocyanate was totally consumed in its reaction with phosphorus pentachloride at 100°, it has to be assumed that monomeric trichlorophosphazene was formed and underwent a further reaction with the isocyanate to give the four-membered ring intermediate

[1] Gumpert, *J. prakt. Chem.*, 1885, **31**, 119.
[2] Kuhle, G.P. 1,094,737; Sayigh and Ulrich, *J.*, 1963, 3146.
[3] Campbell and Monagle, *J. Amer. Chem. Soc.*, 1962, **84**, 1493.
[4] Ulrich and Sayigh, *Angew. Chem.*, 1962, **74**, 900.

(V) which, at higher temperatures, collapsed to di-*o*-tolylcarbodi-imide and phosphorus oxychloride.

Evidence that this type of intermediate may be involved was obtained by repeating the reaction in refluxing tetrachloroethane (145°) with a phosphorus pentachloride–isocyanate ratio of 0·6 : 1. All of the carbonyl chloride generated (34·5%) was produced in



the first half-hour. From the infrared spectrum of this mixture, it was seen that some carbodi-imide had been formed and that some isocyanate remained unchanged. After 2 hours' heating the intensities of the carbodi-imide and the P=O absorption had increased while that of the isocyanate had remained constant.

The results are consistent with the annexed mechanism which starts with attack of the nitrogen atom of the isocyanate on phosphorus pentachloride.

Phenyl isocyanate was found to react with phosphorus pentachloride in the same way as did *o*-tolyl isocyanate, but no carbodi-imide was produced from cyclohexyl and n-butyl isocyanate. Almost quantitative yields of phosphorus oxychloride and in one case 50% yield of the *N*-dichloromethylene amine were isolated.

Experimental.—Infrared spectra were obtained by using a Perkin-Elmer model 21 spectrophotometer.

Reaction of o-tolyl isocyanate with phosphorus pentachloride. (*A*) Without solvent. *o*-Tolyl isocyanate (13·3 g., 0·1 mole) was added to phosphorus pentachloride (25 g., 0·12 mole) and, on heating, vigorous evolution of carbonyl chloride took place. After the mixture had been refluxed for 20 hr. (120—130°) all the isocyanate had been consumed [$\nu_{max.}$ 6·1 (C=N) and 7·75 μ (P=O)]. Phosphorus oxychloride was distilled from the mixture and then *N*-dichloromethylene-*o*-toluidine (II) (1·85 g., 10%), b. p. 52°/0·3 mm., 75°/3 mm., $\nu_{max.}$ (in $CHCl_3$) 6·05 and 11·15 μ. The experiment was repeated and the mixture was refluxed in *o*-dichlorobenzene (200 ml.) for 4 hr [$\nu_{max.}$ 4·75 μ (N·C·N)]. Distillation through a Vigreaux column gave phosphorus oxychloride (6·6 g., 43%) and di-*o*-tolylcarbodi-imide (III) (5·9 g., 53·5%), b. p. 129—131°/0·3 mm., whose i.r. spectrum was identical with that of a sample prepared from di-*o*-tolylthiourea. A residue of 7·2 g. was left.

(*B*) In *o*-dichlorobenzene. Phosphorus pentachloride (25 g., 0·12 mole) was added to *o*-tolyl isocyanate (13·3 g., 0·1 mole) in *o*-dichlorobenzene (100 ml.). On heating, carbonyl chloride was generated and, after 6 hr. under reflux, the mixture was distilled to give di-*o*-tolylcarbodi-imide (4·45 g., 40%), b. p. 138—149°/0·7 mm.

(*C*) In tetrachloroethane. To phosphorus pentachloride (12·5 g., 0·06 mole) in refluxing tetrachloroethane (50 ml.), *o*-tolyl isocyanate (13·3 g., 0·1 mole) was added during 2 hr. The carbonyl chloride generated during this time, and in a further reflux period of 30 min., was bubbled into N-sodium hydroxide. The carbonyl chloride dissolved in the mixture was swept out in a stream of nitrogen. By titration of the sodium hydroxide solution, it was found that 34·5% of the carbonyl chloride (based on phosphorus pentachloride) was formed [$\nu_{max.}$ of the reaction mixture, 4·7 (N=C=N) and 4·42 μ (·NCO)]. Heating for a further 2 hr. produced no more carbonyl chloride [the i.r. spectrum of the reaction mixture showed increased intensity

of the bands at 4·7 and 7·75 μ (P=O) and unchanged intensity of band at 4·42 μ]; the intensity of the band at 4·7 μ reached a maximum after heating for 6 hr., when the mixture was distilled, to give di-*o*-tolylcarbodi-imide (3·2 g., 48%), b. p. 131—135°/0·5 mm.

Reaction of phenyl isocyanate with phosphorus pentachloride. The reaction was carried out as with *o*-tolyl isocyanate, in refluxing *o*-dichlorobenzene. By examination of the i.r. spectrum of the mixture, the reaction was seen to have proceeded to about 50% after 6 hr. and to be complete after 20 hr. [$\nu_{max.}$ 4·7 (N=C=N), 5·95, 11·3 (*N*-dichloromethyleneaniline) 7·7 μ (P=O)]. Distillation afforded phosphorus oxychloride (70%) and a fraction of b. p. 89—151°/1 mm., which was diluted with ethanol and treated with a few drops of dilute hydrochloric acid. *NN'*-Diphenylurea, m. p. 233—235°, separated slowly. This represents a yield of diphenylcarbodi-imide of 11·5%. From the intensity of the N=C=N absorption band, the yield of the carbodi-imide appeared to be 23%. The lower yield of this product compared with that of di-*o*-tolyl-carbodi-imide can be attributed to its lower stability.

Reaction of cyclohexyl isocyanate with phosphorus pentachloride. When cyclohexyl isocyanate (12·5 g., 0·1 mole) was heated with phosphorus pentachloride (25 g., 0·12 mole), reaction began at 40°, with evolution of some carbonyl chloride, and became vigorous at 70—115°. After 30 min. under reflux (120—126°), most of the isocyanate had reacted. After a further 90 min. heating and distillation through a Vigreaux column, phosphorus oxychloride (14 g., 91·5%), a mixture of cyclohexyl isocyanate and *N*-dichloromethylenecyclohexylamine (2·85 g.), and *N*-dichloromethylene cyclohexylamine (9 g., 50%), b. p. 72—73°/9 mm., were obtained [$\nu_{max.}$ (in $CHCl_3$) 6·08, 6·87, 11·05, and 11·6 μ] (Found: N, 71·8. Calc. for $C_7H_{11}Cl_2N$: N, 7·8%). The reaction was repeated in refluxing *o*-dichlorobenzene and again no dicyclohexylcarbodi-imide was detected.

Reaction of n-*butyl isocyanate with phosphorus pentachloride.* The reaction was carried out as with *o*-tolyl isocyanate, in refluxing *o*-dichlorobenzene. After 20 hours' heating, most of the isocyanate had reacted, but no carbodi-imide had been formed. Distillation yielded phosphorus oxychloride (73·8%), but no satisfactory separation of *N*-dichloromethylene-n-butylamine could be achieved.

The authors thank Mr. B. Tucker and Mr. F. Geremia for help with the experiments and in determination of the infrared spectra.

THE CARWIN COMPANY, DIVISION OF THE UPJOHN CO.,
NORTH HAVEN, CONNECTICUT, U.S.A. [*Received, April 16th,* 1963.]

1058. *The Catalytic Action of Anionic Catalysts. Part V.*[1] *The Interaction of Sodium Aromatic Hydrocarbons with Tetraphenylethylene.*

By ALWYN G. EVANS and B. J. TABNER.

IN an earlier publication [2] we gave preliminary results for the reaction of various sodium aromatic hydrocarbons with tetraphenylethylene: we now give details.

Materials.—Tetrahydrofuran, tetraphenylethylene, naphthalene, and phenanthrene were purified as described before.[3] Chrysene, anthracene, and naphthacene (B.D.H. purest grade) and picene, 1,2-benzanthracene, pyrene, perylene, and pentacene, (Light's) were, before use, recrystallised twice from suitable solvents and then sublimed, or degassed, under a high vacuum.

Sodium hydrocarbons were prepared by passing tetrahydrofuran solutions of the aromatic hydrocarbon over a freshly sublimed sodium film.[3] Spectrophotometric measurements showed that in all cases, except that of tetraphenylethylene, only the mononegative ions were formed. In some cases, storage over the sodium film for much longer periods caused dinegative ions to be formed slowly. The filtered solutions were stable, but rather sensitive to heat.

[1] Part IV, *J.*, 1963, 4613.
[2] Evans, Evans, and Tabner, *Proc. Chem. Soc.*, 1962, 338.
[3] (*a*) Evans, Evans, Owen, Tabner, and Bennett, *Proc. Chem. Soc.*, 1962, 226; (*b*) Bennett, Evans, Evans, Owen, and Tabner, *J.*, 1963, 3954.

Measurement of Spectra.—The visible spectra, at room temperature, were measured from 333 to 1000 mμ on Unicam S.P. 500 and S.P. 700 spectrophotometers, with silica cells sealed off from the high-vacuum mixing systems. The electron spin resonance (e.s.r.) spectra, at room temperature, were measured on a Hilger and Watts " Microspin " 9375 Mc./sec. " X "-band spectrometer, with sample tubes sealed off from the high-vacuum mixing systems.

Results.—A known volume of a tetrahydrofuran solution of the sodium hydrocarbon mononegative ion was mixed, under high-vacuum conditions, with a known volume of a tetrahydrofuran solution of tetraphenylethylene. The e.s.r. and visible spectra of the solutions were determined before and immediately after mixing. The transfer of an electron from the tetraphenylethylene negative ion to the aromatic hydrocarbon was studied in the same way. In those systems for which electron transfer occurred, there was an immediate change in

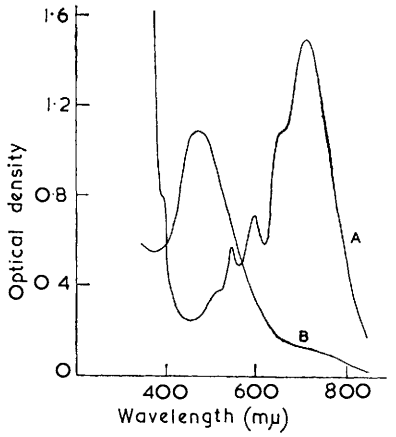


FIG. 1.

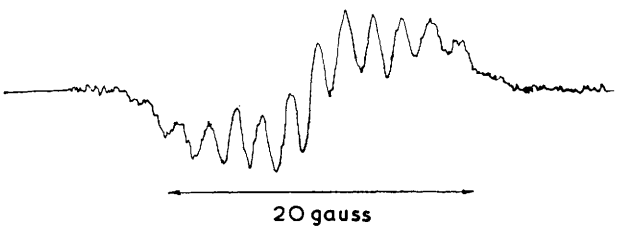


FIG. 2.

FIG. 1. Visible spectra. (A) Solution obtained by mixing 15·13 ml. of a tetrahydrofuran solution of sodium anthracene ($2·85 \times 10^{-3}$ mole $l.^{-1}$) with 1·73 ml. of a tetrahydrofuran solution of tetraphenylethylene ($3·77 \times 10^{-2}$ mole $l.^{-1}$). Optical path-length = 1 mm. This gives the characteristic spectrum of sodium anthracene, showing that no electron transfer occurs.

(B) Solution obtained by mixing 83·27 ml. of a tetrahydrofuran solution of sodium naphthalene ($2·82 \times 10^{-4}$ mole $l.^{-1}$) with 0·738 ml. of a tetrahydrofuran solution of tetraphenylethylene ($8·37 \times 10^{-2}$ mole $l.^{-1}$). Optical path-length = 1 mm. This gives the characteristic spectrum of sodium tetraphenylethylene, showing that electron transfer occurs.

FIG. 2. E.s.r. spectrum of a tetrahydrofuran solution of sodium chrysene ($3·17 \times 10^{-3}$ mole $l.^{-1}$).

TABLE 1.

Ar in $(ArH)^-Na^+$	Colour	Positions of principle maxima ($cm.^{-1}$)
Anthracene	Blue	25·0, 19·5, 18·3, 16·8, 15·1, 13·9 *
1,2-Benzanthracene	Brown	25·8, 25·2, 23·7, 19·9, 18·5, 16·9
Chrysene	Green	26·5, 25·3, 21·4, 20·6, 15·4
Naphthacene	Green	27·8, 24·8, 17·2, 16·5, 15·5, 14·2 *
Naphthalene	Green	27·1, 22·9, 13·6, 12·3 *
Pentacene	Green	26·2, 25·1, 23·2, 22·6, 20·5
Perylene	Blue	17·2, 14·7, 13·2 *
Phenanthrene	Green	25·5, 24·0, 22·5, 15·4, 10·5 *
Picene	Brown	24·7, 22·6, 21·3, 19·9, 14·2
Pyrene	Brown	26·0, 22·0, 20·3, 13·7 *

* See also Balk, Hoijtink, and Schreurs, *Rec. trav. chim.*, 1957, **76**, 813; De Boer and Weissman, *ibid.*, p. 824.

e.s.r. and visible spectrum. Examples of the spectra obtained in these reactions are given in Figs. 1 and 2, and details of the spectra of the aromatic hydrocarbon mononegative ions are given in Table 1. It is seen from Fig. 1 that an electron transfer can be easily followed by

measurement of the visible absorption. The marked difference between the e.s.r. spectrum of the aromatic hydrocarbon mononegative ion, *e.g.*, (chrysene)$^-$ in Fig. 2, and that of the tetraphenylethylene radical ion (given in Part III [3b]) enables the electron transfer to be followed

TABLE 2.

ArH	Electron affinity * (ev)	10^3[Na^+(ArH)$^-$] (mole $l.^{-1}$)	10^3[Olefin] (mole $l.^{-1}$)	Rate of electron transfer
Naphthalene	2·59	0·282	0·742	Rapid
Phenanthrene	2·63	16·5	16·9	Rapid
Chrysene	2·76	2·38	9·35	Rapid
Picene	2·78	1·74	2·06	Rapid
Pyrene	2·96	0·878	6·49	No transfer
1,2-Benzanthracene	3·04	1·37	2·72	No transfer
Anthracene	3·11	2·85	3·87	No transfer
Perylene	3·32	3·27	4·55	No transfer

* Matsen, *J. Chem. Phys.*, 1956, **24**, 602.

TABLE 3.

ArH	Electron affinity * (ev)	10^3[ArH] (mole $l.^{-1}$)	10^3[$Na_2^{2+}(CPh_2{-}CPh_2)^{2-}$] (mole $l.^{-1}$)	Rate of electron transfer
Pyrene	2·96	2·60	1·07	Rapid
1,2-Benzanthracene	3·04	1·02	0·59	Rapid
Anthracene	3·11	2·51	1·15	Rapid
Perylene	3·32	1·86	0·429	Rapid
Naphthacene	3·43	1·66	0·42	Rapid
Pentacene	3·71	Excess	$<\frac{1}{2}$[ArH]	Rapid

* Matsen, *J. Chem. Phys.*, 1956, **24**, 602.

also by the change in e.s.r. spectra. For all the mixed solutions given in Tables 2 and 3, no further change in visible or e.s.r. spectra was noticed over a period of several months.

Discussion.—When the electron is transferred from the sodium aromatic hydrocarbon to the tetraphenylethylene, the equilibrium shown in Part VI is set up.[1] The radical-ion and the di-ion have absorption peaks at 675 and 466 mμ, respectively. When the electron was transferred from the aromatic hydrocarbon to the olefin or from the olefin to the aromatic hydrocarbon, the rate of transfer was too fast to be measured, and, under the conditions of our experiments, the transfer was complete. In no case could we obtain electron transfer in both directions.

Whenever an electron was transferred to tetraphenylethylene, cooling the system to −70° gave the characteristic blue colour of the $Ph_2\dot{C}—\ddot{\bar{C}}Ph_2$ radical ion; these changes with temperature were quite reversible, showing that equilibrium (1) was operating.

When 1,1,3,3-tetraphenylbut-1-ene is used as the olefin and sodium chrysene as the electron-donor, slow but measurable electron-transfer occurs.[2] For tetraphenylethylene the electron-transfer from sodium chrysene is too fast to be measured, even at −68·5°.

Our results show that tetraphenylethylene lies between picene and pyrene in its ability to take up an electron in tetrahydrofuran. We may, in this way, use this series of aromatic hydrocarbons to bracket the ability of a molecule to accept an electron in solution.

The calculated electron affinity values given in the Tables show the same sequence as that demonstrated by our results. A feature of these results lies in their very clear-cut nature; the electron-transfer is very rapid and complete either in one direction or the other, although the aromatic hydrocarbons chosen show a fairly gradual change in their calculated electron affinities. These electron affinities, however, refer to single molecules in the gas phase, whereas our experimental values involve ion pairs in solution. Thus, as we change

the aromatic hydrocarbon we not only change its electron affinity, but also the dissociation energy and heat of solution of the $Na^+(ArH)^-$ ion pair.

We thank the University of Wales for a Research Studentship (to B. J. T.), and D.S.I.R. for a grant to purchase the e.s.r. spectrometer.

CHEMISTRY DEPARTMENT, UNIVERSITY COLLEGE, CARDIFF. [*Received, April 16th*, 1963.]

1059. *Formation of Higher Silanes by the Tetramethylammonium Chloride-catalyzed Disproportionation of Methylchlorodisilanes.*

By JOSEPH V. URENOVITCH, RADE PEJIC, and ALAN G. MACDIARMID.

PREVIOUS investigators [1] have suggested that the less volatile products formed during the tetramethylammonium chloride-catalyzed disproportionation of methylchlorodisilanes might consist of methylchloropolysilanes. The present investigation was carried out in order to see if any higher silanes could be found amongst the reaction products.

In view of the experimental difficulties involved in handling mixtures of only slightly volatile chloropolysilanes, which hydrolyze rapidly, it was considered advisable to convert all the less volatile products of the reaction into completely methylated species by means of methylmagnesium bromide. In this manner the trisilane, $Me_3Si{\cdot}SiMe_2{\cdot}SiMe_3$, and tetrasilane, $Me_3Si{\cdot}[SiMe_2]_2{\cdot}SiMe_3$, were obtained in addition to less volatile oily materials which presumably consisted of higher methylpolysilanes of general formula, $Me_3Si{\cdot}[SiMe_2]_x{\cdot}SiMe_3$. These results therefore support the previous postulate that methylchloropolysilanes are formed in the disproportionation reaction.

In order to test the thermal stability of a simple pure compound containing several silicon atoms joined together, the above-mentioned tetrasilane was heated *in vacuo* at 260° for 7 hr.; no decomposition or reaction of any type occurred.

Experimental.—The mixture of methylchlorodisilanes employed boiled at 150—160° and consisted mainly of $MeSiCl_2{\cdot}SiMeCl_2$ and $MeSiCl_2{\cdot}SiMe_2Cl$.[1,2]

The mixture of methylchlorodisilanes was refluxed with tetramethylammonium chloride, as described by Cooper and Gilbert.[1] After removal of the mixture of mono-, -di-, and trimethylchlorosilanes boiling in the range 57—70°, an excess of an ethereal solution of methylmagnesium bromide was added to the material remaining in the reaction vessel. After refluxing for *ca.* 8 hr., the precipitate was separated by filtration and the ether removed by a rough distillation. Fractionation of the less volatile material on a Podbielniak distilling apparatus (Mini-Cal series 3400) produced, in addition to $Me_3Si{\cdot}SiMe_3$ from unreacted starting material: (*a*) $Me_3Si{\cdot}SiMe_2{\cdot}SiMe_3$, b. p. 175—177°/1 atm., 85·5—87·0°/36·2 mm. (lit., 175—176°/750 mm.[3], 180°/1 atm.[4]), n_D^{20} 1·4559 (lit., 1·4612,[3] 1·4599 [4]) [Found: C, 47·3; H, 11·6; Si, 40·9%; *M* (cryoscopy in C_6H_6), 206. Calc. for $C_8H_{24}Si_3$: C, 47·05; H, 11·75; Si, 41·2%; *M*, 204·5]; (*b*) $Me_3Si{\cdot}[SiMe_2]_2{\cdot}SiMe_3$, b. p. 109—111°/14·5 mm. (lit.,[3] 112—113°/16 mm.), n_D^{20} 1·4874 (lit.,[3] 1·4877) [Found: C, 45·6; H, 11·6%; *M* (cryoscopy in C_6H_6), 256. Calc. for $C_{10}H_{30}Si_4$: C, 45·7; H, 11·5%; *M*, 262·7]; (*c*) a higher-boiling oily liquid which was not identified. This was assumed to consist of higher methylpolysilanes.

The weights of higher silanes recovered were in the ratio

$$Me_3Si{\cdot}SiMe_2{\cdot}SiMe_3 : Me_3Si{\cdot}[SiMe_2]_2{\cdot}SiMe_3 : Me_3Si{\cdot}[SiMe_2]_xSiMe_3 = 1{\cdot}8 : 1{\cdot}0 : 5{\cdot}9.$$

This base-catalyzed disproportionation of methylchlorodisilanes therefore appears to yield mainly compounds in which more than four silicon atoms are linked together.

[1] Cooper and Gilbert, *J. Amer. Chem. Soc.*, 1960, **82**, 5042.
[2] Kumada and Kuriyagawa, Jap. P. 7222, 7223 (1954) (*Chem. Abs.*, 1956, **50**, 10,125).
[3] Wilson and Smith, *J. Org. Chem.*, 1961, **26**, 557.
[4] Graf zu Stolberg, *Angew. Chem.*, internat. edn., 1962, **1**, 510.

A sample of $Me_3Si{\cdot}[SiMe_2]_2{\cdot}SiMe_3$ was sealed *in vacuo* in a small glass tube. It was then immersed completely in an oil bath which was slowly heated to 260° and maintained at this temperature for 7 hr. No observable decomposition occurred. When the tube was opened to a high-vacuum system, no material more volatile than $Me_3Si{\cdot}[SiMe_2]_2{\cdot}SiMe_3$ could be detected. An infrared spectrum of the compound was identical with that recorded before heating.

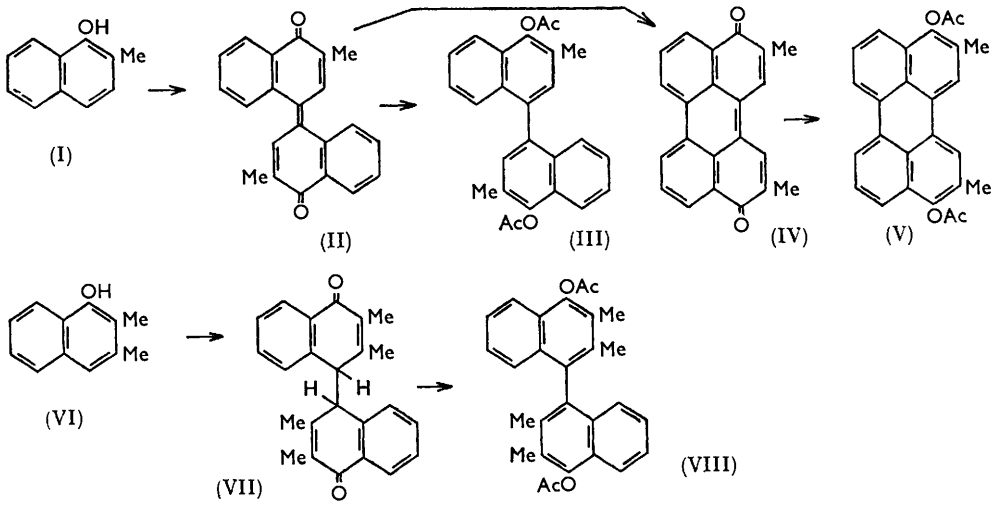
A University of Pennsylvania Undergraduate Research Scholarship (to R. P.) and an Alfred P. Sloan Research Fellowship (to A. G. MacD.) are gratefully acknowledged. This work was, in part, supported by the Advanced Research Projects Agency, Office of the U.S. Secretary of Defense. The sample of mixed methylchlorodisilanes was kindly presented by the General Electric Company, Waterford, New York.

JOHN HARRISON LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA,
PHILADELPHIA 4, U.S.A. [*Received, April 17th,* 1963.]

1060. *A New Perylene Synthesis.*

By B. R. BROWN and A. H. TODD.

SEVERAL perylene syntheses involve stages in which vigorous conditions are used to cause dimerisation of naphthalene derivatives.[1] The natural occurrence of perylenequinones[2] and the observation that extended quinones result from aerial oxidation of phenols in presence of a laccase from *Polyporus versicolor* [3-5] led us to investigate mild methods for the synthesis of perylenes from naphthalenes.

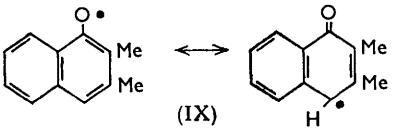


2-Methyl-1-naphthol[6] (I) in an acetate buffer is converted by air in the presence of laccase from *Polyporus versicolor* into 3,3′-dimethyl-1,1′-binaphthyl-4,4′-quinone (II). Aqueous potassium ferricyanide produced the same compound, but chromic acid in acetic

[1] Clar, " Aromatische Kohlenwasserstoffe," 1st edn., Springer-Verlag, Berlin, 1941, p. 221.
[2] Lord Todd, *Experientia*, 1962, **18**, 433; Anderson and Murray, *Chem. and Ind.*, 1956, 376; Batterham and Weiss, *Proc. Chem. Soc.*, 1963, 89.
[3] Bocks, Brown, and A. H. Todd, *Proc. Chem. Soc.*, 1962, 117.
[4] Brown and Bocks in " Enzyme Chemistry of Phenolic Compounds," ed. Pridham, Pergamon Press, Oxford, 1963, p. 129.
[5] Benfield, Bocks, Bromley, and Brown, *Phytochemistry*, in the press.
[6] Lesser, *Annalen*, 1914, **402**, 1.

acid yielded 2-methyl-1,4-naphthaquinone (cf. ref. 6). Reductive acetylation of the quinone (II) gave 4,4′-diacetoxy-3,3′-dimethyl-1,1′-binaphthyl [6] (III). Exposure of a solution of the quinone (II) in concentrated sulphuric acid to visible light at room temperature produced 2,11-dimethylperylene-3,10-quinone (IV) (15%), which on reductive acetylation gave 3,10-diacetoxy-2,11-dimethylperylene (V), identified as a perylene derivative from its characteristic ultraviolet absorption spectrum.

The action of air and the enzyme, or of potassium ferricyanide, on 2,3-dimethyl-1-naphthol (VI) yielded 2,3,2′,3′-tetramethyl-1,1′-dinaphthone (VII) as a monohydrate, the infrared spectrum of which contains a band at 1635 cm.$^{-1}$ characteristic of diones, and weak hydroxyl bands at 3400 and 3520 cm.$^{-1}$; the compound gave no colour with ferric chloride. Acetylation of this diketone (VII) gave 4,4′-diacetoxy-2,3,2′,3′-tetramethyl-1,1′-binaphthyl (VIII). It is of interest that introduction of a second methyl group at the 3-position of the naphthalene nucleus inhibits formation of an extended quinone and gives



(IX)

rise to the dinaphthone (VII). The fact that several dimerised anthracene derivatives occur naturally in the dianthrone form [7] may be connected with this structural difference which causes steric hindrance and prevents formation of a fully planar extended quinone. Isolation of the dinaphthone (VII) also supports a free-radical mechanism postulated for the action of laccase on phenols [5] in which an initial free radical (IX) dimerises to give compound (VII).

Experimental.—Infrared spectra were measured on a Perkin-Elmer 21 spectrophotometer. Alumina was Spence's grade H, 10% deactivated with aqueous acetic acid. Light petroleum refers to the fraction of b. p. 40—60° unless otherwise stated.

3,3′-Dimethyl-1,1′-binaphthyl-4,4′-quinone (II). (*a*) 2-Methyl-1-naphthol (855 mg.) was dissolved in 0·01M-acetate buffer (pH 5·4; 3·5 l.), and the enzyme solution [4,5] (40 ml.) was added. The solution was kept at 30° for 4 days; it became bright pink with a deposit of dark red material. Extraction with chloroform yielded 3,3′-dimethyl-1,1′-binaphthyl-4,4′-quinone which separated from light petroleum (b. p. 60—80°)–benzene as black prisms (544 mg., 63%), $\lambda_{max.}$ (in $CHCl_3$) 254, 316, and 492 mμ, $\nu_{max.}$ (in $CHCl_3$) 860, 890, 935, 1020, 1100, 1170 1260, 1300, 1370, 1450, 1510, 1590, and 1620 cm.$^{-1}$. Good analyses could not be obtained for this compound since complete removal of solvent from it resulted in a change of form to a brown powder which showed hydroxyl absorption in the infrared spectrum.

(*b*) 2-Methyl-1-naphthol (200 mg.) in ethanol (10 ml.) was added dropwise during 5 min. to a stirred solution of potassium ferricyanide (1·25 g.) and sodium hydroxide (0·1 g.) in water (30 ml.). The solution became bright red. After 2 hr. at room temperature, a dark red precipitate of crude 3,3′-dimethyl-1,1′-binaphthyl-4,4′-quinone (196 mg.) was separated, washed with water, and dried. The ultraviolet and infrared spectra of this compound were identical with those of that obtained by enzymic oxidation.

4,4′-Diacetoxy-3,3′-dimethyl-1,1′-binaphthyl (III). Crude 3,3′-dimethyl-1,1′-binaphthyl-4,4′-quinone (315 mg.; from enzymic oxidation) in redistilled acetic anhydride (25 ml.) was boiled under reflux for 2 hr. with an excess of zinc dust, then filtered hot. The residue was extracted with hot acetic anhydride (25 ml.). The combined filtrate and extract were poured into water (100 ml.), and the precipitate was separated, washed with water, and dried. The precipitate was taken up in light petroleum–benzene (4 : 1 v/v) and adsorbed on alumina (30 g.). Elution with the same solvent mixture yielded 4,4′-diacetoxy-3,3′-dimethyl-1,1′-binaphthyl (159 mg., 39%) which separated from chloroform–methanol as colourless plates, m. p. 240—241° (Found:

[7] *E.g.*, The sennosides, see Thomson, "Naturally Occurring Quinones," Butterworths, London, 1957, p. 180.

C, 78·3; H, 5·6. Calc. for $C_{26}H_{22}O_4$: C, 78·4; H, 5·6%), $\lambda_{max.}$ (in $CHCl_3$) 244, 294, and 323 mμ (log ε 3·40, 3·33, and 2·77). Lesser [6] gives m. p. 235—236°.

Crude 3,3′-dimethyl-1,1′-binaphthyl-4,4′-quinone (308 mg.) from the ferricyanide oxidation, treated in the same way, yielded the same diacetate (243 mg., 62%), m. p. and mixed m. p. 239—240°.

2,11-*Dimethylperylene*-3,10-*quinone* (IV). 3,3′-Dimethyl-1,1′-binaphthyl-4,4′-quinone (257 mg.) was dissolved in concentrated sulphuric acid (60 ml.), to give a dark green solution ($\lambda_{max.}$ 662 mμ). The solution was irradiated with visible light from a tungsten lamp, with water-cooling of the flask. After 40 hr., the solution had become cherry-red ($\lambda_{max.}$ 512 mμ). The sulphuric acid was diluted with water (350 ml.), and the product extracted into *s*-tetrachloroethane. The organic phase was washed with water, dried ($CaCl_2$), and evaporated, to yield a yellow solid (38 mg., 15%). Extraction from a porous thimble with hot nitromethane yielded 2,11-*dimethylperylene*-3,10-*quinone* as orange needles (Found: C, 84·7; H, 4·6. $C_{22}H_{14}O_2$ requires C, 85·1; H, 4·55%), $\lambda_{max.}$ [in $(CHCl_2)_2$] 249, 254, 264, 315, 333, 348, 367, and 433 mμ (log ε 3·20, 3·19, 3·19, 2·91, 2·65, 2·86, 2·94, and 3·57), $\lambda_{min.}$ 260, 278, 325, 337, 356, and 373 mμ (log ε 3·13, 2·67, 2·57, 2·62, 2·74, and 2·87), $\lambda_{infl.}$ 292—308 and 408—415 mμ (log ε 2·79 and 3·44), $\nu_{max.}$ (in Nujol) 711, 763, 819, 888, 966, 1026, 1208, 1239, 1287, 1339, 1589, 1612, and 1639 cm.$^{-1}$.

3,10-*Diacetoxy*-2,11-*dimethylperylene* (V). 3,3′-Dimethyl-1,1′-binaphthyl-4,4′-quinone (152 mg.) in concentrated sulphuric acid (75 ml.) was irradiated for 40 hr. with visible light from a tungsten lamp. The solution was poured on ice, and the resulting suspension was centrifuged. The solid was washed with water and methanol and dried. This crude 2,11-dimethylperylene-3,10-quinone with redistilled acetic anhydride (20 ml.) and an excess of zinc dust was boiled under reflux for 2 hr., then filtered hot. The residue was extracted with hot acetic anhydride (20 ml.). The combined filtrate and extract were poured into water (50 ml.), and crude 3,10-diacetoxy-2,11-dimethylperylene separated as greyish-brown needles (40 mg.). These were taken up in light petroleum–benzene (1 : 1 v/v) and adsorbed on alumina (5 g.). Elution with benzene yielded 3,10-*diacetoxy*-2,11-*dimethylperylene* (24 mg., 12%) which separated from light petroleum (b. p. 60—80°)–benzene as orange prisms which changed to needles at 260—265° and melted at 281—283° (Found: C, 78·7; H, 5·4. $C_{26}H_{20}O_4$ requires C, 78·8; H, 5·1%); it had $\lambda_{max.}$ (in $CHCl_3$) 296, 396, 419, and 446 mμ (log ε 3·53, 4·09, 4·42, and 4·52), $\lambda_{min.}$ 335, 403, and 431 mμ (log ε 3·14, 4·05, and 4·18), $\lambda_{infl.}$ 375—379 mμ (log ε 3·72), and $\nu_{max.}$ (in Nujol) 718, 753, 769, 802, 858, 868, 905, 960, 1010, 1050, 1076, 1095, 1159, 1205, 1239, 1580, 1600, 1625, and 1750 cm.$^{-1}$.

2,3-*Dimethyl*-1-*naphthol* (VI). 2,3-Dimethyl-1-naphthylamine (5·0 g.) (prepared as described by Willstaedt [8] except that 2,3-dimethyl-1-nitronaphthalene was reduced to the amine by hydrogenation over Raney nickel) was dissolved in ethanol (100 ml.), and a 40% solution (20 ml.) of fluoroboric acid in water added. The solution was cooled to 0° and ethyl nitrite (4 ml.) added with stirring. After 5 min., crystals of 2,3-dimethylnaphthalene-1-diazonium fluoroborate were formed and cold ether (70 ml.) was then added. The crystals were separated, washed with ether, and dried in a vacuum-desiccator to yield the fluoroborate as pale yellow needles (6·8 g., 86%).

All the diazonium fluoroborate was dissolved in water (500 ml.), and ether (200 ml.) was added. After 16 hr. at room temperature, the phases were separated, and the ethereal solution was washed with water and dried. Removal of the ether yielded a red oil which, after crystallisation from light petroleum, yielded 2,3-dimethyl-1-naphthol as colourless needles (1·9 g., 38%), m. p. 83—84°. Cocker [9] gives m. p. 84°.

2,3,2′,3′-*Tetramethyl*-1,1′-*dinaphthone* (VII). (*a*) 2,3-Dimethyl-1-naphthol (320 mg.) was dissolved in 0·01M-acetate buffer (pH 5·0; 4 l), and the enzyme solution (20 ml.) was added. After 4 days at 30°, further enzyme solution (20 ml.) was added. After a further 4 days at 30°, the solution was extracted with chloroform, and the chloroform solution washed with water and dried. Evaporation of the solution to small bulk and addition of ether yielded 2,3,2′,3′-*tetramethyl*-1,1′-*dinaphthone monohydrate* (160 mg., 51%) as colourless needles, m. p. 155° (Found: C, 79·6; H, 6·6. $C_{24}H_{22}O_2,H_2O$ requires C, 80·0; H, 6·7%), $\lambda_{max.}$ (in EtOH) 259 mμ (log ε 3·025), $\lambda_{infl.}$ 280—295 mμ (log ε 2·715), $\nu_{max.}$ (in Nujol) 660, 697, 711, 748, 773, 788, 806, 970, 1007, 1114, 1161, 1198, 1242, 1261, 1308, 1331, 1574, 1598, 1635, 3400, and 3520 cm.$^{-1}$. An ethanolic solution of the compound gave no colour with aqueous ferric chloride.

[8] Willstaedt, *Svensk kem. Tidskr.*, 1942, **54**, 223.
[9] Cocker, *J.*, 1946, 36.

(*b*) 2,3-Dimethyl-1-naphthol (101 mg.) in ethanol (10 ml.) was added to a stirred solution of potassium ferricyanide (0·6 g.) and sodium hydroxide (0·1 g.) in water (30 ml.). After 2 hr. at room temperature, the mixture was extracted with chloroform, and the organic phase was washed with water and dried. Removal of the chloroform yielded a colourless solid (30 mg., 30%) which was recrystallised from chloroform–methanol to give 2,3,2′,3′-tetramethyl-1,1′-dinaphthone hydrate as colourless needles, m. p. and mixed m. p. 153°.

4,4′-Diacetoxy-2,3,2′,3′-tetramethyl-1,1′-binaphthyl (VIII). 2,3,2′,3′-Tetramethyl-1,1′-dinaphthone (206 mg.), dry pyridine (3 ml.), and redistilled acetic anhydride (12 ml.) were kept at 60° for 24 hr. The mixture was poured into water (60 ml.) and extracted with ether (2 × 50 ml.). The ethereal solution was washed with dilute hydrochloric acid (3 × 100 ml.) and water, and dried. Removal of the ether yielded a pale brown solid (184 mg.) which was taken up in light petroleum–benzene (4 : 1 v/v) and adsorbed on alumina (20 g.). Elution with light petroleum–benzene (7 : 3 v/v) yielded *4,4′-diacetoxy-2,3,2′,3′-tetramethyl-1,1′-binaphthyl* (172 mg., 70%) which recrystallised from aqueous methanol as prisms, m. p. 198—203° (decomp.) (Found: 78·9; H, 6·1. $C_{28}H_{26}O_4$ requires C, 78·8; H, 6·15%), $\lambda_{max.}$ (in EtOH) 236 and 289 mμ (log ε 5·02 and 4·88), $\lambda_{infl.}$ 278—281 and 295—300 mμ (log ε 4·79 and 4·82), $\nu_{max.}$ (in Nujol) 725, 758, 767, 856, 891, 903, 1012, 1075, 1167, 1204, 1223, 1332, 1492, 1595, and 1745 cm.$^{-1}$.

We thank the D.S.I.R. for a maintenance grant (to A. H. T.) and Miss Sheila M. Bocks for preparing the enzyme solution.

DYSON PERRINS LABORATORY,
THE UNIVERSITY, OXFORD.

[*Received, April 20th,* 1963.]

1061. *Conversion of Acetates into Alcohols in* 1,3-*Diol Systems.*

By J. G. PRITCHARD and R. L. VOLLMER.

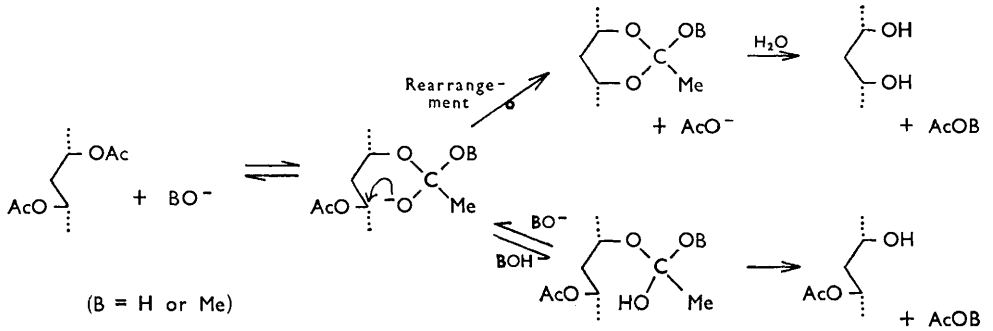
THE possible occurrence of rearrangements in the sequence of configurations of the substituent groups along the hydrocarbon chain during the " hydrolysis " of poly(vinyl acetate) to poly(vinyl alcohol) has been pointed out by Bunn [1] and further by Arcus [2] who has proposed a route *via* a cyclic intermediate to account for the supposed rearrangement. This matter has not received attention since 1955, as far as we are aware, and is of continuing importance.[3]

Conversion of poly(vinyl acetate) into poly(vinyl alcohol) is most commonly carried out by sodium hydroxide catalysis in methanol and proceeds at least partly without consumption of alkali and with the production of methyl acetate.[4-8] Hence, the more important reaction and possible rearrangement to be considered involve the ester-interchange shown in the scheme below for the case in which B = Me. A major contribution from reaction *via* hydroxide ion (*i.e.*, hydrolysis; B = H) would be expected to enter only for aqueous methanol solutions in which a large excess of sodium hydroxide was employed.

In conditions covering both the above situations, we have now studied the base-catalysed conversion into diols of the model systems *meso*- and racemic 2,4-diacetoxypentane, and find that no detectable rearrangement occurs. This result accords with

[1] Bunn, *J.*, 1947, 305; *Nature*, 1948, **161**, 929.
[2] Arcus, *J.*, 1955, 2801.
[3] Cf. Fujii *et al.*, *Chem. High Polymers* (*Japan*), 1962, **19**, 120, 124; Okamura, Kodama, and Higashimura, *Makromol. Chem.*, 1962, **53**, 180.
[4] Blaikie and Crozier, *Ind. Eng. Chem.*, 1936, **28**, 1155.
[5] McDowell and Kenyon, *J. Amer. Chem. Soc.*, 1940, **62**, 415.
[6] Minsk, Priest, and Kenyon, *J. Amer. Chem. Soc.*, 1941, **63**, 2715.
[7] Beresniewicz, *J. Polymer Sci.*, 1959, **39**, 63.
[8] Horiuchi, *Rev. Phys. Chem., Japan*, 1941, **15**, 71, and references cited therein.

the observation that, for similar five-membered-ring cases, orthoester formation accompanied by Walden inversion occurs only for reactions in alcoholic media when the leaving group is more readily ionisable than acetate (*e.g.*, halide or toluene-*p*-sulphonate).[9]



We can find no evidence that the behaviour of our model systems and the polymer system should be mechanistically or kinetically very different,[6,10] and we conclude that no configurational rearrangement should occur during the polymer conversion and that polymer properties should be interpreted accordingly.

Experimental.—The preparation of the pentane-2,4-diol diacetate isomers and their properties have been described, and isomeric mixtures can be analysed conveniently by vapour-phase chromatography.[11] These diacetates were boiled for 2 hr. in two types of basic medium that are commonly used for poly(vinyl acetate)–poly(vinyl alcohol) conversion:[4-7] (*a*) a *ca.* three-fold excess of sodium hydroxide (2N) in commercial methanol (wet with *ca.* 3% of water), and (*b*) a catalytic quantity of sodium (15 mole % of the diacetate; 0·02N) in dry methanol (dried by magnesium and iodine,[12] kept over CaO). Solutions (*a*) were neutralised with acetic acid, precipitated sodium acetate was filtered off, and the solvent was removed *in vacuo*. The residual pentane-2,4-diol was esterified with acetic anhydride, and the ester was isolated conventionally and distilled without fractionation, a centre cut being taken for chromatographic analysis. Solutions (*b*) were fractionated with a high reflux ratio. The first fractions were shown by vapour-phase chromatography to contain methyl acetate, which was not present in the original methanol. The remaining solution was then worked up as for (*a*). The diacetates were compared chromatographically with the initial samples of diacetate isomers and showed that in no case did the processes described above cause structural change, within the 1% estimated possible error in the reproducibility of the chromatograms. It is already known that the esterification step in this system does not involve rearrangement.[11]

CHEMSTRAND RESEARCH CENTER, INC.,
DURHAM, NORTH CAROLINA, U.S.A. [*Received, April 25th*, 1963.]

[9] Isbell, *Ann. Rev. Biochem.*, 1940, **9**, 70; Winstein *et al.*, *J. Amer. Chem. Soc.*, 1942, **64**, 2787, 2796; 1943, **65**, 613; 1946, **68**, 119; 1948, **70**, 812.
[10] Smith and Olsson, *Z. phys. Chem.* (*Leipzig*), 1922, **103**, 26; Skrabal and Hugetz, *Monatsh.*, 1926, **47**, 17; Lee and Sakuranda, *Z. phys. Chem.* (*Leipzig*), 1939, **184**, *A*, 268.
[11] Pritchard and Vollmer, *J. Org. Chem.*, 1963, **28**, 1545.
[12] Lund and Bjerrum, *Ber.*, 1931, **64**, 210.

1062. 2,3-*Dimethyl*-4(1H)-*quinolone*.

By Paul J. Scheuer and Frank Werny.

Recently we isolated 1,2-dimethyl-4-quinolone, with several furoquinoline alkaloids, from the bark and leaves of the endemic Hawaiian shrub *Platydesma campanulata* Mann (Rutaceae).[1] This substance was first encountered among several non-crystalline chromatographic fractions which produced spots of R_F 0·2 when the thin-layer chromatograms were sprayed with modified Dragendorff's reagent.[2] The respective fractions were subsequently combined and transformed into the yellow picrate of a base, $C_{11}H_{11}NO,C_6H_3N_3O_7$, m. p. 234—236° (decomp. 237°) (after recrystallization from ethanol). The free base, regenerated by column chromatography on aluminium oxide G and recrystallized from chloroform–light petroleum, had m. p. 178—179°, with a crystalline transition at 174°.

The ultraviolet spectrum pointed to a 2-methyl-4-quinolone.[3] The nuclear magnetic resonance (n.m.r.) spectrum of the natural product (kindly determined by Professor L. Mandell, Emory University) did not allow an immediate choice between 1,2- and 2,3-dimethyl-4-quinolone and favoured the 2,3-dimethyl assignment by ascribing a one-proton peak at 6·05 δ to the vinylogous lactam proton attached to nitrogen. We therefore synthesized 2,3-dimethyl-4-quinolone.

The literature contains several syntheses of the 2,3-dimethyl compound but some discrepancies among reported melting points. Most of the melting points fall in the range 300—330°,[4a–e] but Lions and his co-workers[5] report m. p. 217°. We synthesized 2,3-dimethyl-4-quinolone by condensation of anthranilic acid with butan-2-one and subsequent ring closure according to Niementowski's procedure[6] and obtained white crystals, having m. p. 305—307° (decomp.) after two recrystallizations from ethanol. An identical product resulted from base-catalyzed ring closure of *o*-acetamidopropiophenone. The n.m.r. spectrum of this compound,[7] which was clearly not identical with our natural product, exhibited, in liquid sulphur dioxide, two three-proton peaks (2·1 and 2·48 δ) assigned to the 3- and the 2-methyl group, respectively. No signal corresponding to the amide proton could be detected under the required conditions of solvent and concentration.

N.m.r. signals of alkylated 4-quinolones.

	1-	2-	3-	Solvent
1,2-Dimethyl	3·59	2·34		$CDCl_3$
2,3-Dimethyl		2·48	2·10	SO_2
1,2,3-Trimethyl	3·52	2·30	2·07	$CDCl_3$

We subsequently synthesized from 2,3-dimethyl-4-quinolone, by methylation with dimethyl sulphate, 1,2,3-trimethyl-4-quinolone, m. p. 188—189°. The methyl peaks of this compound in deuteriochloroform produced signals at 2·07, 2·30, and 3·52 δ. Comparison of the n.m.r. signals in the Table shows correct assignments for the three methyl

[1] F. Werny, Ph.D. Diss., University of Hawaii, 1962.
[2] Robles, *Pharm. Weekblad*, 1959, **94**, 178.
[3] Ewing and Steck, *J. Amer. Chem. Soc.*, 1946, **68**, 2181; Steck, Ewing, and Nachod, *J. Amer. Chem. Soc.*, 1949, **71**, 238.
[4] (*a*) Conrad and Limpach, *Ber.*, 1891, **24**, 2990, m. p. 305°; (*b*) Wohnlich, *Arch. Pharm.*, 1913, **251**, 526 (*Chem. Abs.*, 1914, 8, 1110), m. p. *ca.* 330°; (*c*) Mander-Jones and Trikojus, *J. Proc. Roy. Soc. New South Wales*, 1932, **66**, 300, m. p. 315°; (*d*) Plant and Rosser, *J.*, 1929, 1867, m. p. 319—320°; (*e*) Buu-Hoï and Royer, *J.*, 1948, 106, m. p. 310° (picrate, m. p. 227°).
[5] Gillis, Lions, and Ritchie, *J. Proc. Roy. Soc. New South Wales*, 1940, **73**, 258.
[6] Niementowski, *Ber.*, 1894, **27**, 1394.
[7] Measured by Dr. R. E. Moore of this Department.

groups. The one-proton peak at 6·05 δ (see above) which was originally assigned to the amide hydrogen must therefore be correctly assigned to the 3-hydrogen atom of the 1,2-dimethyl compound.

Experimental.—Analyses by Dr. A. Bernhardt, Mülheim/Ruhr, Germany. Melting points taken on a micro hot stage. Ultraviolet spectra were measured on a Beckman DK-2, infrared spectra on a Beckman IR-5, and n.m.r. spectra on a Varian A-60 instrument.

2,3-*Dimethyl*-4-*quinolone*. (*a*) Niementowski's procedure [6] was adapted to this preparation as follows. Butan-2-one (100 g., 1·35 moles) and anthranilic acid (100 g., 0·73 mole) were heated in a 3-necked flask (500 ml.) equipped with an immersed thermometer and a downward condenser above an air-cooled reflux condenser. The mixture was held at 90° for 0·5 hr. and then at 190—200° for 1·5 hr. The white precipitate formed on cooling was removed, washed with boiling benzene, and recrystallized from 95% ethanol (m. p. *ca.* 295°; 7 g., 5·5%). Two further recrystallizations raised the m. p. to 305—307° (decomp.).

(*b*) Freshly distilled propiophenone (67 g., 0·5 mole) was nitrated as described by Zenitz and Hartung.[8] The resulting *o*-nitropropiophenone, after removal of the crystalline *m*-isomer, was distilled at 180°/20 mm. The resulting oil was hydrogenated in benzene solution with 10% palladium–charcoal at 42 lb. per sq. in. for 5 hr. After removal of the catalyst the benzene solution of *o*-aminopropiophenone was immediately treated with acetic anhydride and acetic acid. During 2 hr. on the steam-bath the benzene was distilled off and the resulting mixture was poured into water. A green oil separated and crystallized overnight at 0°. After recrystallization from aqueous ethanol it had m. p. 70·5—71·5° (reported,[4b] 71°) (7·4 g., 7·7% from propiophenone) (Found: C, 69·0, 69·1; H, 6·8, 6·7. Calc. for $C_{11}H_{13}NO_2$: C, 69·1; H, 6·8%).

o-Acetamidopropiophenone (7 g., 0·037 mole) was refluxed for 3 hr. on the steam-bath with aqueous-ethanolic sodium hydroxide. After removal of the ethanol the crystalline 2,3-dimethyl-4-quinolone separated (3·7 g., 58%); it was identical with the compound prepared from anthranilic acid and butanone (Found: C, 76·4, 76·5; H, 6·3, 6·5; N, 8·2; active H, 0·58. Calc. for $C_{11}H_{11}NO$: C, 76·3; H, 6·4; N, 8·1; 1 active H, 0·58%); $\lambda_{max.}$ (2·89 × 10^{-5}M in 95% EtOH) (log ε in parentheses) 335·4 (4·09), 327·4 (4·08), 292·4sh (3·44), 279sh (3·27), 245·8 (4·46), 238·2 (4·49), $\lambda_{min.}$ 328·7 (4·03), 256·8 (3·14), 221 (4·17); $\lambda_{max.}$ (2·89 × 10^{-5}M in 0·01N-HCl in 95% EtOH) 335·6sh (3·50), 321 (3·81), 309·9 (3·83), 281·7sh (3·97), 267·2sh (3·40), 246sh (4·19), 232 (4·62), 212 (4·37); $\lambda_{min.}$ 256·4 (3·24), 219·4 mμ (4·33). The n.m.r. spectrum, for a liquid sulphur dioxide solution, with tetramethylsilane as internal standard showed three-proton singlets at 2·10 and 2·48 δ, three aromatic protons in a complex multiplet centred at 7·50 δ, and complex multiplet representing a single proton centred at 8·2 δ.

1,2,3-*Trimethyl*-4-*quinolone*. *N*-Methylation was carried out by adapting the procedure of Drummond and Lahey.[9] To a solution of potassium hydroxide (0·5 g., 0·009 mole) in methanol (30 ml.), 2,3-dimethyl-4-quinolone (1 g., 0·006 mole) was added. The solvent was evaporated and an excess of dimethyl sulphate (10 ml.) was added slowly. After ½ hour's heating on the steam-bath, the excess of dimethyl sulphate was destroyed by adding 40% aqueous potassium hydroxide to pH 10. The aqueous solution was extracted with chloroform; the extract was dried (Na_2SO_4) and evaporated. The residue was recrystallized twice from benzene, to yield the *product* (590 mg., 31%) as colourless prisms, m. p. 188—189° (Found: C, 76·5, 76·6; H, 7·2, 7·0. $C_{12}H_{13}NO$ requires C, 77·0; H, 7·0%); $\lambda_{max.}$ (in 5·4 × 10^{-5}M-EtOH) (log ε in parentheses) 344·5 (4·06), 331·6 (4·04), 293sh (3·18), 281·9 (3·05), 269·7 (2·97), 249—243 (4·39—4·42), 214 (4·36); $\lambda_{min.}$ 337·3 (4·00), 264·2 (2·87), 224·4 (4·02); $\lambda_{max.}$ (5·4 × 10^{-5}M in 0·01N-HCl in 95% EtOH) 344·9 (3·72), 327 (3·87), 317·4 (3·85), 247·2 (4·29), 236·7 (4·50), 214 (4·30); $\lambda_{min.}$ 339·7 (3·72), 323·3 (3·85), 260·8 (2·87), 223 mμ (3·91). N.m.r. signals in deuteriochloroform (tetramethylsilane as internal standard) indicated three-proton peaks at 2·07, 2·30, and 3·52 δ; three aromatic protons in a septet centred about 7·32 δ, and one aromatic proton as a doublet at 8·30 δ.

1,2-*Dimethyl*-4-*quinolone*. The n.m.r. spectrum in deuteriochloroform (with tetramethylsilane, as above) included three-proton peaks at 2·34 and 3·59 δ; one-proton singlet at 6·05 δ, three aromatic protons in a poorly resolved septet centred about 7·39 δ, and a one-proton doublet centred about 8·36 δ.

[8] Zenitz and Hartung, *J. Org. Chem.*, 1946, **11**, 444.
[9] Drummond and Lahey, *Austral. J. Sci. Research A.*, 1949, **2**, 630.

The authors express their gratitude to the National Science Foundation and to the National Institutes of Health for financial support.

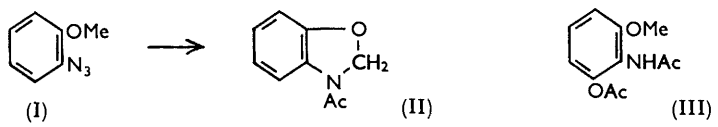
DEPARTMENT OF CHEMISTRY, UNIVERSITY OF HAWAII,
HONOLULU 14, HAWAII, U.S.A.

[*Received, April 29th*, 1963.]

1063. *Pyrolysis of Aryl Azides in Acetic Anhydride.*

By R. K. SMALLEY and H. SUSCHITZKY.

WE have recently [1] obtained acylbenzimidazoles by decomposing aryl azides with suitable *ortho*-substituents in acid anhydrides. However, no cyclisation took place [2] when under similar conditions *o*-methoxyphenyl azide (I) was pyrolysed in acetic anhydride with the intention of preparing a benzoxazole derivative (II). A small quantity of the diacetyl compound (III) had formed instead. Similarly, thermolysis of phenyl azide and several



(I) (II) (III)

of its simple derivatives in acetic anhydride produced *o*-aminophenols in addition to the usual products of such decompositions, namely, amines and azo-compounds. Formation of *o*-aminophenols has so far not been observed on pyrolysis of aromatic azides, though it was recently reported [3] to occur to a small extent in the photolysis of phenyl azide in glacial acetic acid. *p*-Aminophenol, on the other hand, is a recognised product of decomposition of phenyl azide in aqueous acid.[4] It arises undoubtedly from interaction of the intermediate imino-radical ($R\cdot\dot{N}:$) and water, to give phenylhydroxylamine which isomerises readily to *p*-aminophenol under the prevailing conditions.

The results from the various decompositions of aryl azides are collected in the Table. Aminophenols were obtained by solvent-extraction or by chromatographic separation of their acetyl derivatives followed by hydrolysis. The nitrophenyl azides behaved

Products of decomposition of aryl azides in boiling acetic anhydride (15 hr.)

Azide, $R\cdot N_3$		$2\text{-}NH_2\cdot C_6H_3<^{X}_{OH\text{-}1}$		$R\cdot N{:}N\cdot R$	$R\cdot NH_2$	
R	g.	X	%	%	%	Other products (%)
Ph *	15	H	18·1	9·3	20·7	—
o-Me·C_6H_4	15	3-Me	46·0	1·0	33	—
p-Me·C_6H_4	15	5-Me	41·5	1·3	25·2	—
o-Cl·C_6H_4	11	3-Cl	21·8	4·5	19	—
p-Br·C_6H_4	12	5-Br	22·6	3·3	17·5	—
1-$C_{10}H_7$	7	(1-NH_2·$C_{10}H_6$·OH-2)	20	4·3	28·5	—
o-NO_2·C_6H_4	15	—	—	—	—	Benzofuroxan, 80·5
m-NO_2·C_6H_4	10	—	—	—	—	(Unchanged, 33·5)
p-NO_2·C_6H_4	10	—	—	—	—	(Unchanged, 35·6)

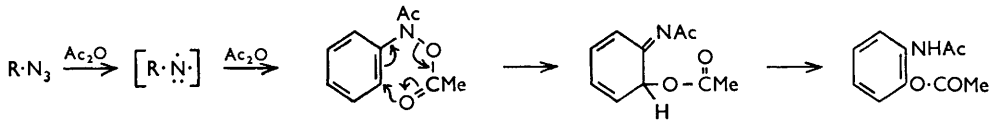
* Similar results were obtained in propionic anhydride.

differently: the *ortho*-isomer gave only the expected benzofuroxan, while the *meta*- and *para*-compounds decomposed very slowly with evolution of brown fumes, leaving intractable

[1] Meth-Cohn, Smalley, and Suschitzky, *J.*, 1963, 1666.
[2] Meth-Cohn, unpublished work.
[3] Horner, Christmann, and Gross, *Chem. Ber.*, 1963, **96**, 399.
[4] Griess, *Ber.*, 1886, **19**, 313.

residues. By contrast, decomposition of *m*-nitrophenyl azide in sulphuric acid is believed [5] to yield a mixture of 2-amino-4-nitro- and 4-amino-2-nitro-phenol, while that of the *para*-isomer gave 2-amino-5-nitrophenol.[6]

Formation of acylated *o*-aminophenols by decomposition of azides in acetic anhydride probably occurs by rearrangement of *ON*-diacylphenylhydroxlyamines. These can feasibly arise by interaction of the biradical intermediate (R·N:) with the solvent. Migration of an acyloxy-group ($R{\cdot}CO_2$) into the *ortho*-position of a benzene ring when *ON*-diacylphenylhydroxylamines are heated in a solvent has in fact been described [7] and its mechanism is probably analogous to that of a Claisen rearrangement. Moreover, we observed that phenylhydroxylamine itself yields *o*-aminophenol, as well as the expected diacetylphenylhydroxylamine, when heated in acetic anhydride. The steps in the conversion of phenyl azide into the *o*-acetamidophenyl acetate can be visualised to take place as set out (R = Ph).



Experimental.—Preparation and decomposition of azides. Azides were prepared as previously [1] described and purified by distillation *in vacuo*. Decomposition was effected in boiling acetic anhydride (4 times the weight of azide) for 15 hr.

In a typical procedure the solvent (60 ml.) was removed *in vacuo* from the reaction mixture in which phenyl azide (15 g.) had decomposed. The residue was extracted with light petroleum (b. p. 100—120°), leaving a carbonaceous residue which was discarded. The extract deposited, on slow evaporation, *o*-diacetylaminophenyl acetate, m. p. 75° undepressed on admixture with an authentic sample.[8] The mother-liquor was chromatographed through an alumina column. Elution with benzene gave azobenzene, with chloroform acetanilide, and with ethanol *o*-hydroxyacetanilide in that order. Products were identified by mixed m. p.s and infrared analyses. The stated (Table) yield of *o*-aminophenol was obtained by hydrolysis of the various acetylated fractions. During the chromatographic separation a hot zone was observed to travel down the column. This was found to be due to partial hydrolysis of polyacetylated aminophenol on alumina to give monoacetyl compounds. Products of all the experiments mentioned in the Table were worked up in a similar way.

2-*Acetamido*-3-*methoxyphenyl acetate*, obtained from *o*-methoxyphenyl azide, had m. p. 138° (Found: C, 59·1; H, 5·6. $C_{11}H_{13}NO_4$ requires C, 59·2; H, 5·8). Hydrolysis gave the *aminophenol*, m. p. 123° (Found: C, 60·3; H, 6·5. $C_7H_9NO_2$ requires C, 60·4; H, 6·5%).

6-*Diacetylamino*-m-*tolyl acetate* (OAc = 1), obtained from *p*-tolyl azide, had m. p. 83—84° (Found: C, 62·6; H, 6·3. $C_{13}H_{15}NO_4$ requires C, 62·6; H, 6·05%). Extraction, with light petroleum, of the decomposition products of *p*-bromophenyl azide deposited 2-*acetamido*-5-*bromophenyl acetate*, m. p. 128° (Found: C, 44·4; H, 4·05. $C_{10}H_{10}BrNO_3$ requires C, 44·1; H, 3·7%).

We thank Parke, Davis & Co. for a research fellowship (to R. K. S.), and Mr. D. Hall for some experimental assistance.

ROYAL COLLEGE OF ADVANCED TECHNOLOGY, SALFORD, LANCS. [*Received, May 9th*, 1963.]

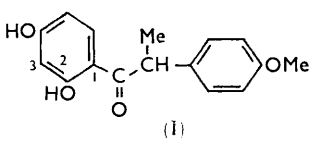
[5] Kehrmann and Idzkowska, *Ber.*, 1899, **32**, 1065.
[6] Friedlander and Zeitlin, *Ber.*, 1894, **27**, 196; 1895, **28**, 1386.
[7] Horner and Steppan, *Annalen*, 1957, **606**, 24.
[8] Diepolder, *Ber.*, 1911, **44**, 2500.

1064. *Extractives of* Afrormosia elata.

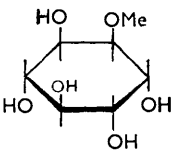
By C. D. Foxall and J. W. W. Morgan.

McMurry and Theng described the isolation and characterisation of the isoflavone, afrormosin,* from the acetone extract of afrormosia heartwood.[1] We now find this extract to contain also (−)-angolensin (I) and 1-*O*-methyl-(+)-inositol (II), a new cyclitol.

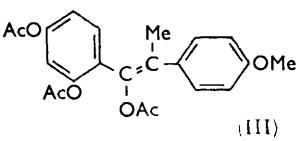
Angolensin occurs in the heartwood of *Pterocarpus angolensis* [2] (with the isoflavone muningin) and in *P. indicus* [3] and *P. erinaceus*.[4] The angolensin obtained from afrormosia was identified by comparison with a sample from *P. angolensis*, both samples being lævorotatory. Racemisation was effected by aqueous sodium hydroxide in 2 hours at room temperature, or in 10 minutes at the b. p., but, contrary to an earlier report,[3] not by sodium carbonate at room temperature. The active and the inactive form lead to two series of derivatives which are not clearly distinguished in the literature; these are described in the Experimental section. It is of particular interest that whilst acetylation of (−)- and (±)-angolensin by acetic anhydride–pyridine gives (−)- and (±)-diacetates, acetic anhydride–sodium acetate affords a single inactive triacetate (III). The triacetate arises by enolisation and acetylation of the carbonyl group, a conclusion confirmed by the presence of an infrared band at 1680 cm.$^{-1}$ in the spectra of the diacetates which is absent from that of the triacetate.



(I)



(II)



(III)

The cyclitol $C_7H_{14}O_6$ formed a penta-acetate, and with boiling hydriodic acid gave (+)-inositol (characterised as its hexabenzoate). It is, therefore, a mono-*O*-methyl-(+)-inositol. Of the three possible isomers, 3-*O*-methyl-(+)inositol (pinitol) is well known and different. Further, the new compound is not enantiomeric with 2-*O*-methyl-(−)-inositol (quebrachitol). It must, therefore, be 1-*O*-methyl-(+)-inositol which hitherto was unknown as a natural substance. In support of this, its physical constants are in agreement with its being the enantiomer of 1-*O*-methyl-(−)-inositol which has been synthesised by Angyal and Matheson.[5]

Experimental.—Extraction of afrormosia *heartwood.* Afrormosia sawdust (4·7 kg.) was extracted successively by boiling light petroleum, ether, and acetone for 20 hr. each. On concentration of the acetone extract (1 l.) and cooling, crystals of crude afrormosin (4 g.) separated. Recrystallisation from ethanol–acetone gave afrormosin (1·4 g.), m. p. 226—228° (acetate, m. p. 170—172°; *O*-methyl ether, m. p. 179—181°, which did not depress the m. p. of an authentic sample [1,6]).

On further concentration of the acetone extract and cooling to 0° a black syrup (230 g.) separated. The supernatant liquor, which was mainly aqueous, was evaporated to a brown syrup (27 g.) which, when stirred with methanol, left crystals of the new cyclitol (7·5 g.) undissolved. From the black syrup, ether leached a yellow syrup which was further extracted with benzene; the evaporated benzene extract was then extracted repeatedly with boiling light

* The second "r" in *Afrormosia* is sometimes incorrectly omitted. The name "afrormosin" is therefore used in place of the previous [1] "afromosin."

[1] McMurry and Theng, *J.*, 1960, 1491.
[2] King, King, and Warwick, *J.*, 1952, 1920.
[3] Gupta and Seshadri, *J. Sci. Ind. Res., India*, 1956, **15**, *B*, 146.
[4] Akisanya, Bevan, and Hirst, *J.*, 1959, 2679.
[5] Angyal and Matheson, *J. Amer. Chem. Soc.*, 1955, **77**, 4343.
[6] Eade, Hinterberger, and Simes, *Austral. J. Chem.*, 1963, **16**, 188.

petroleum (b. p. 80—100°). A semicrystalline paste (44 g.) was thus removed, which was finally purified by chromatography (in several portions) on silica in benzene. Elution by benzene–ether (9 : 1) gave a solid which crystallised from benzene–light petroleum, giving (−)-angolensin (15·6 g.), m. p. 120·5—121°, $[\alpha]_D^{20}$ −115° (*c* 2·5 in $CHCl_3$) (Found: C, 70·8; H, 6·0; OMe, 11·3. Calc. for $C_{16}H_{16}O_4$: C, 70·6; H, 5·9; OMe, 11·4%). Mixed m. p. and infrared comparison showed the sample to be identical with authentic (−)-angolensin, $[\alpha]_D$ −115° (in $CHCl_3$), obtained from muninga. Angolensin did not give a green colour with nitric acid.

Racemisation of angolensin. (−)-Angolensin (2 g.) in aqueous N-sodium hydroxide (100 ml.) was boiled for 15 min. The solution was cooled and acidified, and the product was isolated in ether. The syrup obtained crystallised from light petroleum (b. p. 80—100°), and crystallised from benzene–light petroleum to give (±)-*angolensin* (1·3 g.), m. p. 86·5—88°, $[\alpha]_D$ ±0° (Found: C, 70·8; H, 6·1%). The infrared spectra (in $CHCl_3$) of (−)- and (±)-angolensin were identical. The inactive form, m. p. 119—120°, described by Gupta and Seshadri [3] was not obtained.

Another racemisation was carried out at room temperature, with the above quantities, and followed polarimetrically: $[\alpha]_D^{19}$ +215° (5 min.); +141° (15 min.); +88° (30 min.); +36° (1 hr.); +4° (2 hr.). When N-sodium carbonate was used in place of sodium hydroxide, the values obtained were: $[\alpha]_D^{19}$ +59° (5 min.); +56° (15 min.); +55° (30 min.); +54° (1 hr.); +53° (3 hr.).

Methyl ethers of angolensin. (−)-Angolensin and an excess of diazomethane in ether–methanol gave (−)-4-O-*methylangolensin*, m. p. 62·5—63·5°, $[\alpha]_D^{20}$ −142° (*c* 2 in $CHCl_3$) (Found: C, 71·2; H, 6·4; OMe, 20·4. $C_{17}H_{18}O_4$ requires C, 71·3; H, 6·3; OMe, 21·7%), as blades from methanol. Similarly (±)-angolensin gave (±)-4-*O*-methylangolensin, m. p. 70·5—71·5°, $[\alpha]_D$ ±0°, whose infrared spectrum (in CCl_4) was identical with that of the (−)-form. King, King, and Warwick [2] described an *O*-methylangolensin, m. p. 71°, of unspecified activity. Both monomethyl ethers gave a green solution in concentrated nitric acid.

(−)-Angolensin (1 g.), anhydrous potassium carbonate (5 g.), and dimethyl sulphate (2·5 ml.) in acetone (50 ml.) were boiled for 4 hr. The mixture was filtered and the filtrate evaporated, treated with ammonia diluted with water, and extracted into ether. Evaporation of the ether gave a syrup which was passed in benzene through a column of alumina. The eluted compound crystallised from light petroleum (b. p. 40—60°) as needles of (−)-*di*-O-*methylangolensin* (0·6 g.), m. p. 50—51°, $[\alpha]_D^{22}$ +26° (*c* 2 in $CHCl_3$) (Found: C, 71·8; H, 6·6; OMe, 28·1. $C_{18}H_{20}O_4$ requires C, 72·0; H, 6·7; OMe, 31·0%), $\nu_{max.}$ (in CCl_4) 1660 cm.$^{-1}$. Similar methylation of (±)-angolensin gave a syrupy dimethyl ether.

Acetates of angolensin. (±)-Angolensin and acetic anhydride–pyridine at room temperature or the b. p. gave (±)-*angolensin diacetate*, m. p. 88·5—89·5° (Found: C, 67·5; H, 5·9; OAc, 24·8. $C_{20}H_{20}O_6$ requires C, 67·5; H, 5·7; OAc, 24·2%), $\nu_{max.}$ (in CCl_4) 1680 and 1760 cm.$^{-1}$, as prisms from light petroleum. (−)-Angolensin, by the same method, gave (−)-*angolensin diacetate*, b. p. 210°/0·1 mm., $[\alpha]_D^{15}$ −82° (*c* 2 in $CHCl_3$) (Found: C, 67·1; H, 5·7; OAc, 21·0%), as a syrup. The compounds had identical infrared spectra except for an extra peak at 1640 cm.$^{-1}$ in that of the (−)-compound. Gupta and Seshadri [3] have described the isolation of an optically inactive diacetate, m. p. 94°, from both (−)- and (±)-angolensin.

Both (−)- or (±)-angolensin with boiling acetic anhydride–sodium acetate (1 hr.) afforded *angolensin triacetate*, m. p. 129·5—131° (Found: C, 66·1; H, 5·5; OAc, 31·5. $C_{22}H_{22}O_7$ requires C, 66·3; H, 5·6; OAc, 32·4%), $\nu_{max.}$ (in $CHCl_3$) 1750 cm.$^{-1}$, as prisms from methanol. A form, m. p. 103—104°, obtained in the first experiment was converted into the higher-melting form by recrystallisation and seeding; both forms were optically inactive.

Angolensin triacetate (0·18 g.) in methanol (10 ml.) containing concentrated hydrochloric acid (3% by vol.) was boiled for 1 hr. The product, precipitated by addition of water and recrystallised from benzene–light petroleum, was (±)-angolensin, m. p. and mixed m. p. 86—88°, $[\alpha]_D$ ±0°.

1-O-*Methyl*-(+)-*inositol.* Recrystallisation of the crude compound from aqueous ethanol gave prisms of the *cyclitol*, m. p. 207—208°, $[\alpha]_D^{22}$ +60·7° (*c* 2 in H_2O) (Found: C, 42·9; H, 7·2; OMe, 13·0. $C_7H_{14}O_6$ requires C, 43·3; H, 7·3; OMe, 16·0%). The compound gave a *penta-acetate*, m. p. 110·5—111·5°, $[\alpha]_D^{19}$ +29·1° (*c* 2 in $CHCl_3$), +32·8° (*c* 4 in EtOH) (Found: C, 50·2; H, 6·0. $C_{17}H_{24}O_{11}$ requires C, 50·5; H, 6·0%). Angyal and Matheson [5] give m. p. 207°, $[\alpha]_D^{18}$ −58° (in H_2O) for 1-*O*-methyl-(−)-inositol and m. p. 111°, $[\alpha]_D^{15}$ −31° (in EtOH) for its penta-acetate.

The physical constants of pinitol and quebrachitol[7] are different from those of our ether and they have distinct infrared spectra.

The 1-methyl ether (0·5 g.) in hydriodic acid (7·5 ml.; *d* 1·7) was boiled for 1 hr. After evaporation *in vacuo* the residue was digested with methanol. Crystals were collected and recrystallised from ethanol as (+)-inositol, m. p. and mixed m. p. 248—249°, $[\alpha]_D^{20}$ +65·7° (*c* 2 in H_2O) {hexabenzoate, m. p. and mixed m. p. 252—253°, $[\alpha]_D^{24}$ +64·5° (*c* 2 in H_2O)}. The infrared spectra of (+)-inositol and its hexabenzoate were identical with those of authentic samples.

The authors gratefully acknowledge the help of Dr. T. B. H. McMurry and Professor S. J. Angyal in supplying authentic samples.

FOREST PRODUCTS RESEARCH LABORATORY, PRINCES RISBOROUGH, AYLESBURY, BUCKS. [*Received, May 13th*, 1963.]

[7] Angyal and Anderson, *Adv. Carbohydrate Chem.*, 1959, **14**, 135.

1065. *Solvent Shifts of Nuclear Spin Coupling Constants due to Hydrogen Bonding.*

By D. F. EVANS.

UNLIKE chemical shifts, nuclear-spin coupling constants are normally virtually independent of the solvent, except where changes in conformational equilibria are involved. The present Note reports solvent effects for ^{13}C–H and F–H coupling constants.

Chloroform forms weak complexes with many polar molecules, and it seems likely that C–H · · · X hydrogen bonds are present.[1-3] Appreciable differences in J^{13}_{C-H} (given below, for simplicity, as J_{C-H}) are observed for solutions of chloroform in various solvents (Table 1). The values show little correlation with the dipole moments or dielectric constants of the solvents. There is, however, a qualitative relation between the increase in J_{C-H} (relative to the " inert " solvent cyclohexane) and the ability of the solvent molecules to enter into hydrogen bonding. Except for benzene,[4] a measure of this ability is provided by the chemical shifts δ given in Table 1. The correlation between J_{C-H} and δ

TABLE 1.

^{13}C–H coupling constants and proton chemical shifts (relative to tetramethylsilane as an internal reference) of chloroform in various solvents.

Solvent	J_{C-H} (c./sec.) * Mole fraction of $CHCl_3$ = 0·15	δ (p.p.m.) Mole fraction of $CHCl_3$ = <0·01	Solvent	J_{C-H} (c./sec.) * Mole fraction of $CHCl_3$ = 0·15	δ (p.p.m.) Mole fraction of $CHCl_3$ = <0·01
Cyclohexane	208·1	7·09	Et_3N	214·2	8·32
CCl_4	208·4	7·24	MeOH.....	214·3	7·92
$CHCl_3$	209·5	7·26	MeCN	214·6	7·58
C_6H_6	210·6	(6·16)	$COMe_2$	215·2	8·01
AcCl.....	211·8	7·42	H·CO·NMe_2	217·4	8·35
$MeNO_2$	213·6	7·54	Me_2SO.....	217·7	8·31
Et_2O	213·7	7·81			

* ±0·3 c./sec.

is only approximate, but some of the discrepancies may be partly due to the errors involved in using chemical shifts as an indication of the strength of fairly weak hydrogen bonds.[3,5]

[1] Huggins, Pimentel, and Shoolery, *J. Chem. Phys.*, 1955, **23**, 896, 1244.
[2] Lord, Nolin, and Stidham, *J. Amer. Chem. Soc.*, 1955, **77**, 1365.
[3] Howard, Jumper, and Emerson, *J. Mol. Spectroscopy*, 1963, **10**, 117.
[4] Reeves and Schneider, *Canad. J. Chem.*, 1957, **35**, 251.
[5] Hatton and Richards, *Trans. Faraday Soc.*, 1961, **57**, 28.

However, it is unlikely that the comparatively low value of J_{C-H} for the triethylamine solution can be explained in this way, since a variety of evidence [1] indicates that the chloroform–triethylamine complex is particularly stable.

C–H coupling constants in different compounds have been the subject of much experimental and theoretical work.[6] For unsubstituted hydrocarbons there is, as expected on the basis of the Fermi contact term, a good correlation between J_{C-H} and the *s*-character of the C–H bond. For sp^3-, sp^2-, and *sp*-hybridization, the values of J_{C-H} are approximately 125, 157, and 250 c./sec., respectively. Electronegative substituents (as in chloroform itself), increase J_{C-H}, and recent work [6] suggests that this is mainly due to a corresponding increase in the *s*-character of the C–H bond. Assuming an electrostatic model for the $Cl_3CH \cdots X$ hydrogen bond, we may consider two effects resulting from the formation of this bond. These effects will not act independently, but it is convenient to consider them separately. First, as a consequence of electrostatic repulsion, the electrons of the C–H bond will tend to move closer to the carbon atom. This will increase the *s*-character of this bond (cf. Coulson [7]), and hence the ^{13}C–H coupling constant will also increase. Secondly, the C–H bond may lengthen. This would be expected to oppose the increase in *s*-character caused by the first effect.

The marked increase in J_{C-H} when chloroform is involved in hydrogen bonding suggests that the first effect is dominant. It is significant that the C–D stretching frequency of $CDCl_3$ is virtually the same in ether and acetone solutions as in inert solvents such as cyclohexane.[1,2] This indicates that in the first two solvents hydrogen bonding involves no appreciable change in the C–D bond length. The infrared spectra of $CDCl_3$, in dimethyl sulphoxide and *NN*-dimethylformamide were measured, and only small decreases in the C–D stretching frequency were observed [$\nu(C_6H_{12})$ 2253 cm.$^{-1}$, $\nu(H{\cdot}CO{\cdot}NMe_2)$ 2239 cm.$^{-1}$, $\nu(Me_2SO)$ 2221 cm.$^{-1}$, $\Delta\nu/\nu(H{\cdot}CO{\cdot}NMe_2) = -0{\cdot}6\%$, $\Delta\nu/\nu(Me_2SO) = -1{\cdot}4\%$]. However, in triethylamine solution, the effect is much more marked [$\Delta\nu/\nu(Et_3N) = -3{\cdot}7\%$].[1] The lengthening of the C–D bond which this implies may account for the rather low ^{13}C–H coupling constant of chloroform in this solvent, which was mentioned above. That non-specific polar effects are not very important is indicated by the ^{13}C–H coupling constants found for methyl iodide in carbon tetrachloride and *NN*-dimethylformamide solutions. (J_{C-H} in $CCl_4 = 150{\cdot}7 \pm 0{\cdot}2$ c./sec., J_{C-H} in $H{\cdot}CO{\cdot}NMe_2 = 151{\cdot}5 \pm 0{\cdot}2$ c./sec., mole fraction of $CH_3I = 0{\cdot}10$).

The acetylenic C–H bond is known to form hydrogen bonds which are roughly comparable in strength with those found for chloroform.[5,8] Nevertheless, for phenylacetylene only a small increase in J_{C-H} was observed in going from carbon tetrachloride solution to dimethyl sulphoxide solution ($J_{C-H} = 250{\cdot}8 \pm 0{\cdot}3$ c./sec. in CCl_4, $252{\cdot}0 \pm 0{\cdot}3$ c./sec. in Me_2SO; mole fraction of phenylacetylene = 0·15). On the basis of the above discussion this may be connected with the fact that, in contrast to deuteriochloroform, the acetylenic C–H stretching frequency is considerably decreased by hydrogen bonding.[8] For phenylacetylene in dimethyl sulphoxide, $\Delta\nu/\nu$ (relative to a cyclohexane solution) was found to be $-4{\cdot}1\%$.*

The present work is mainly concerned with differences in coupling constants rather than the absolute values themselves. Nevertheless, it may be noted the ^{13}C–H coupling constant for pure chloroform given above ($209{\cdot}5 \pm 0{\cdot}3$ c./sec.) is in fair agreement with that reported by Tiers [9] ($209{\cdot}17 \pm 0{\cdot}09$ c./sec.). The ^{13}C–H,^{12}C–H isotopic chemical shift was found to be $0{\cdot}005_7$ p.p.m., which agrees with Tiers's value of 0·0059 p.p.m., but not with the

* The reasons for this marked difference in infrared behaviour are not clear.

[6] Juan and Gutowsky, *J. Chem. Phys.*, 1962, **37**, 2198; Muller, *ibid.*, 1962, **36**, 359, and references therein.

[7] Coulson, " Valence," Oxford University Press, 2nd edn., 1961.

[8] Brand, Eglinton, and Morman, *J.*, 1960, 2526; West and Kraihanzel, *J. Amer. Chem. Soc.*, 1961, **83**, 765, and references therein.

[9] Tiers, *J. Phys. Chem.*, 1960, **64**, 373.

value of 0·0021 p.p.m. obtained by Dreeskamp and Samann.[10] The ^{13}C–H coupling constant of methyl iodide in carbon tetrachloride (150·7 ± 0·2 c./sec.) is close to that found by Frei and Bernstein[11] (150·8 ± 0·2 c./sec.). These authors also report small solvent effects for this coupling constant.

Bromochlorofluoromethane forms hydrogen bonds in a similar manner to chloroform. In this case, hydrogen bonding produces small but definite decreases in the F–H coupling

TABLE 2.

F–H coupling constants and proton chemical shifts (relative to tetramethylsilane as an internal reference) of bromochlorofluoromethane in various solvents.

Solvent	J_{H-F} (c./sec.) * Mole fraction of $CHBrClF = 0·05$	δ (p.p.m.) Mole fraction of $CHBrClF = <0·01$	Solvent	J_{H-F} (c./sec.) * Mole fraction of $CHBrClF = 0·05$	δ (p.p.m.) Mole fraction of $CHBrClF = <0·01$
Cyclohexane	$52·1_0$	7·43	Et_2O	$51·1_2$	8·07
$MeNO_2$	$51·5_6$	7·86	Et_3N	$50·8_3$	8·41
MeCN	$51·4_3$	7·87	Me_2SO	$50·6_7$	8·46
$COMe_2$	$51·1_8$	8·26			

* ±0·1 c./sec. (relative accuracy).

constant (Table 2). The order of solvents is similar to, but not identical with, that found for chloroform. However, the solvent effects for bromochlorofluoromethane are quite small, and the factors involved in F–H coupling constants are not well understood.

Experimental.—Proton magnetic resonance spectra were measured on a Varian V4311 spectrometer at 26° ± 2° and a frequency of 56·45 Mc./sec., and the infrared spectra on a Grubb-Parsons Spectromaster grating spectrometer. The solvents were pure commercial materials, used either directly (normally after drying over Linde molecular sieves) or after purification by standard procedures. The (alcohol-free) chloroform, phenylacetylene, and methyl iodide contained ^{13}C in natural abundance. Signal-to-noise considerations precluded the study of more dilute solutions of these compounds.

INORGANIC CHEMISTRY RESEARCH LABORATORIES,
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON S.W.7.

[*Received, May 16th,* 1963.]

[10] Dreeskamp and Samann, *Z. phys. Chem.* (*Frankfurt*), 1961, **27**, 136.
[11] Frei and Bernstein, *J. Chem. Phys.*, 1963, **38**, 1216.

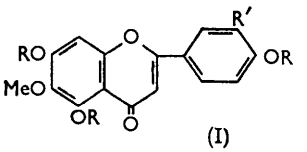
1066. 5,7,4′-*Trihydroxy*-6-*methoxyflavone, a Minor Pigment from* Digitalis lanata, *L.*

By G. O. P. DOHERTY, N. B. HAYNES, and W. B. WHALLEY.

WE recently described[1] the isolation of 5,7,4′-trihydroxy-6,3′-dimethoxyflavone (I; R = H, R′ = OMe) from a crystalline, yellow fraction obtained from the leaves of *D. lanata* L., during the preparation of the cardiac glycosides. Through the courtesy of Messrs. Burroughs Wellcome & Co., we have investigated a more crude pigment fraction from the same source. The principal constituent of this fraction is the same flavone, a minor component is 5,7,4′-trihydroxy-6-methoxyflavone (I; R = R′ = H), the natural occurrence of which has not previously been reported. Isolation of the latter in a pure state was not possible but, after methylation of the mixed pigments, 5,6,7,4′-tetramethoxyflavone (I; R′ = H, R = Me) was readily separated from the 5,6,7,3′,4′-pentamethoxyflavone[1] (I; R = Me, R′ = OMe), by column chromatography.

[1] ApSimon, Haynes, Sim, and Whalley, *J.*, 1963, 3780.

The constitution of the minor ether was established by degradation to *p*-anisic acid and 2-hydroxy-4,5,6-trimethoxyacetophenone and by comparison with an authentic specimen. Its orientation was proved by ethylation of the crude pigment to a mixed



(I)

product which was separated by thin-layer chromatography into 5,7,4′-triethoxy-6,3′-dimethoxyflavone[1] (the major component), 5,7,4′-triethoxy-6-methoxyflavone[2] (I; R′ = H, R = Et), and a small quantity of a third component of flavonoid character which has not been identified.

Experimental.—*5,6,7,4′-Tetramethoxyflavone.* Attempts to separate the constituents from the mixture remaining after removal of the cardiac glycosides from *D. lanata* L., by thin-layer and column chromatography, were unsuccessful.

The crude pigment mixture (3 g.) in boiling acetone (300 ml.) containing potassium carbonate (30 g.) and methyl sulphate (9 g.) was methylated during 4 hr. After isolation, the crude mixture of methylated pigments was chromatographed from benzene on alumina (150 g.). Elution with benzene gave a product which was crystallised from ether–acetone to yield 5,6,7,4′-tetramethoxyflavone (0·3 g.), m. p. 162—163° [Found: C, 66·6; H, 5·3; OMe, 35·8. Calc. for $C_{15}H_6O_2(OMe)_4$: C, 66·6; H, 5·3; OMe, 35·8%], identical with a synthetic specimen (lit.,[3] m. p. 162—163°). Removal of the residual material from the column by elution with acetone gave 5,6,7,3′,4′-pentamethoxyflavone (1·0 g.).

Degradation of 5,6,7,4′-tetramethoxyflavone (0·95 g.) by the method used [1] for 5,6,7,3′,4′-pentamethoxyflavone gave 2-hydroxy-4,5,6-trimethoxyacetophenone which was characterised as the *p*-nitrobenzoate, m. p. 124°, and 2,4-dinitrophenylhydrazone, m. p. 179°, identical with authentic specimens; [1] the acidic component was *p*-anisic acid (0·2 g.), m. p. 185°.

5,7,4′-Triethoxy-6-methoxyflavone. The mixture of crude pigments (2 g.) in acetone (200 ml.) containing potassium carbonate (10 g.) and ethyl iodide (8 ml.) was refluxed for 24 hr. The clarified solution was evaporated (20 ml.) and diluted with water and the yellow prisms (1·5 g.), m. p. 130—150°, were collected. This material was separated by thin-layer chromatography, on Kieselgel G, on 8″ × 8″ glass plates with a 1 mm. layer of adsorbent. The ethylated mixture (10 mg.) in acetone (5 ml.) was placed on a plate as a series of overlapping spots. The plates were developed with chloroform during ½ hr.; the positions of the spots were observed in ultraviolet light. After development the three principal spots were separated mechanically and the adsorbed pigment was removed with warm chloroform. Recovery was ~90% and in this manner the mixture of ethylated pigments (1 g.) was separated by running 100 plates and further purifying the three major fractions by the same process, to give materials A (80 mg.), B (310 mg.), and C (280 mg.). Fraction A was not further investigated: B was identical (m. p., mixed m. p., and infrared spectrum) with 5,7,4′-triethoxy-6,3′-dimethoxyflavone; [1] C, which formed prisms, m. p. 144°, from acetone (Found: C, 68·5; H, 6·4. Calc. for $C_{22}H_{24}O_6$: C, 68·7; H, 6·3%) was identified (m. p., mixed m. p., and infrared spectrum) as 5,7,4′-triethoxy-6-methoxyflavone by comparison with an authentic specimen, prepared by the method of Rangaswami and Venkata Rao.[2]

We thank Drs. T. Dewing and H. T. Openshaw for the supply of crude pigments. Financial assistance was provided by the Government Grants Committee of the Royal Society, The Department of Scientific and Industrial Research, and Imperial Chemical Industries Limited.

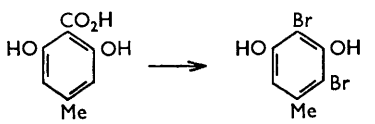
THE DEPARTMENT OF ORGANIC CHEMISTRY, THE UNIVERSITY, LIVERPOOL.
THE SCHOOL OF PHARMACY, THE UNIVERSITY, LONDON. [*Received, May 20th*, 1963.]

[2] Rangaswami and Rao, *Proc. Indian Acad. Sci.*, 1961, **54**, *A*, 51.
[3] Sastri and Seshadri, *Proc. Indian Acad. Sci.*, 1946, **23**, *A*, 262.

1067. *Electrophilic Displacement of Carboxyl in* p-*Orsellinic Acid.*

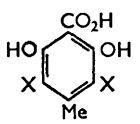
By H. J. Rylance.

The reaction of 2,6-dihydroxy-4-methylbenzoic acid (*p*-orsellinic acid) (I) with bromine to give 2,4-dibromo-orcinol (II) with displacement of the carboxyl group was described by Wagenhofer,[1] and Sarkanen and Dence [2] have described electrophilic displacements of the type (III) ⟶ (IV) (R = CHO, CH_2·OH, or CO_2H). In some work in this Department the halogenation of *p*-orsellinic acid was investigated but our results did not accord with Wagenhofer's. We found that bromination of *p*-orsellinic acid under his conditions gave the 3,5-dibromo-*p*-orsellinic acid (Va) and chlorination gave the corresponding dichloro-acid (Vb) (this could be obtained more easily by using sulphuryl chloride). The structure of the dibromo-compound (Va) was proved by its infrared spectrum and by decarboxylation to the corresponding 2,6-dibromo-orcinol. The dichloro-acid (Vb) was decarboxylated similarly to the dichloro-orcinol.

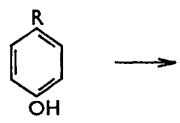


(I)

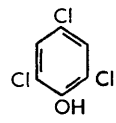
(II)



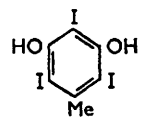
(Va: X = Br, b: X = Cl)



(III)



(IV)



(VI)

However, when the preparation of the corresponding di-iodo-acid was attempted (by using iodine monochloride) electrophilic displacement occurred and tri-iodo-orcinol (VI) was obtained.* 2,4,6-Tri-iodo-orcinol was prepared by Stenhouse[3] in 1865 by the action of iodine monochloride on orcinol. No m. p. or yield was given but the analysis shows that it was tri-iodo-orcinol. Materials prepared by Stenhouse's and our method gave no depression in a mixed m. p. determination. Our method gives the easier working-up and better product.

The displacement that occurs with iodine chloride and not with chlorine or bromine is presumably due to the greater electrophilic character of I^+. In the experiments of Sarkanen and Dence, carried out in the presence of dilute mineral acid or in aqueous acetic acid solutions, the attacking species would presumably be Cl^+ (or $ClOH_2^+$), a more powerful electrophilic agent than the molecular species.

Experimental.—Infrared spectra were measured with a Perkin-Elmer Infracord spectrophotometer and potassium bromide discs.

3,5-*Dibromo*-p-*orsellinic acid.* To *p*-orsellinic acid monohydrate [4] (10 g.) in ether (100 ml.), bromine (6·2 ml.) was added dropwise. Next morning the ether was removed and the *dibromo-acid* recrystallised from ethanol–water; it had m. p. 209—210° (8·7 g.) (Found: C, 29·4; H, 1·8; Br, 49·5. $C_8H_6Br_2O_4$ requires C, 29·4; H, 1·8; Br, 49·1%), $\nu_{max.}$ 1647 (C=O group in acids showing internal hydrogen bonding) and 1212 cm.$^{-1}$ (CO_2H), with weak absorptions between 2500 and 2675 cm.$^{-1}$ characteristic of a strongly hydrogen-bonded OH group.

The working-up was modified in later experiments, the ethereal solution being poured into

* Since submission of this Note, a similar preparation, using iodine–potassium iodide in acetate buffer at pH 4·6, has been noted (Fukamauchi, Enohara, and Uehara, *J. Pharm. Soc. Japan*, 1961, **81**, 294).

[1] Wagenhofer, *Monatsh.*, 1925, **45**, 225.
[2] Sarkanen and Dence, *J. Org. Chem.*, 1960, **25**, 715.
[3] Stenhouse, *Annalen*, 1865, **134**, 212.
[4] Robertson and Robinson, *J.*, 1927, 2199.

water, the ether separated, and the acid extracted from it into sodium hydrogen carbonate solution. The dibromo-acid was obtained by acidification of the alkaline solution with dilute hydrochloric acid.

3,5-*Dichloro*-p-*orsellinic acid.* To *p*-orsellinic acid monohydrate (9·3 g.) in ether (50 ml.), sulphuryl chloride (9 ml.) was added dropwise. Next morning working-up as for the dibromo-compound gave material of m. p. 212·5—214° (4·5 g.) (Found: C, 40·4; H, 2·7; Cl, 29·5. Calc. for $C_8H_6Cl_2O_4$: C, 40·5; H, 2·5; Cl, 30·0%). This has been prepared by Hassall and McMorris [5] by a less direct method.

2,6-*Dibromo-orcinol.* 3,5-Dibromo-*p*-orsellinic acid (5 g.) was refluxed with 0·1N-sodium hydroxide (45 ml.) for 30 hr. On cooling, the *dibromo-orcinol* (1·8 g.) separated and was recrystallised from ethanol–water (charcoal) to give material of m. p. 124—125° (Found: C, 29·8; H, 2·1; Br, 56·6. $C_7H_6Br_2O_2$ requires C, 29·8; H, 2·1; Br, 56·7%).

2,6-*Dichloro-orcinol* This was obtained by the same procedure as above; it had m. p. and mixed m. p. (with material prepared by chlorination of orcinol) 162·5—164° (Found: C, 43·35; H, 3·2; Cl, 36·9. Calc. for $C_7H_6Cl_2O_2$: C, 43·5; H, 3·1; Cl, 36·8%).

2,4,6-*Tri-iodo-orcinol.* To *p*-orsellinic acid monohydrate (10 g.) in ether (250 ml.), iodine monochloride (20 g.) was added dropwise. After being left overnight the solution was extracted with aqueous sodium hydrogen carbonate; on acidification the tri-iodo-orcinol was precipitated. (The presence of three iodine atoms in the molecule greatly enhanced the acidity of the phenolic groups, making the compound soluble in the bicarbonate solution.) The *product* (14 g.), m. p. 161—164° (decomp.), crystallised from ethanol–water (Found: C, 16·8; H, 1·1; I, 76·1. $C_7H_5I_3O_2$ requires C, 16·7; H, 1·0; I, 75·9%). Similar results were obtained on using glacial acetic acid as solvent.

The author thanks Miss M. M. Dickson for the spectroscopic determinations.

EDINBURGH PHARMACEUTICAL INDUSTRIES LIMITED,
WHEATFIELD ROAD, EDINBURGH 11. [*Received, June 12th,* 1963.]

[5] Hassall and McMorris, *J.*, 1959, 2831.