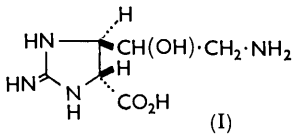
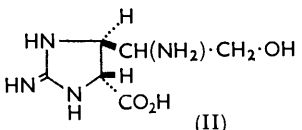
805. *The Structure of Streptolidine.*

By J. H. Bowie, E. Bullock, and A. W. Johnson.

Two recent publications [1,2] have discussed the structure of the antibiotic streptothricin. Hydrolysis of streptothricin gave, among other products, a cyclic guanidine, $C_6H_{12}N_4O_3$, which has been variously named streptolidine,[3] geamine,[4] and roseonine.[5] The American authors [6] have suggested that the structure of streptolidine is (I) and they formulate the side-chain with a terminal amino-group on the basis of the production of a small amount of glycine on oxidation of streptolidine [5] and the production of a *C*-methyl group (<1 mol.)



(I)



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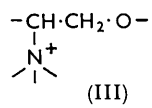

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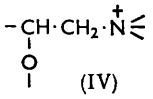

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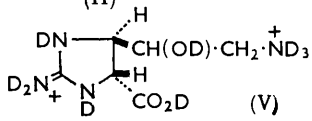


(V)

after reductive deamination. Our interpretation [1] of the nuclear magnetic resonance spectrum of streptolidine led us to favour structure (II). A re-examination of the nuclear magnetic resonance spectrum of streptolidine dihydrochloride and those of the salts of some simple related amino-alcohols has now led us to abandon structure (II) in favour of the American suggestion (I).

Experimental.—Nuclear magnetic resonance spectra were measured on an AEI RS2 instrument operating at 60 Mc./sec. and were calibrated by the side-band technique. The chemical-shift values are quoted in p.p.m. from the HOD absorption which is taken as an arbitrary zero (the position of this band is not necessarily absolutely constant, but since the solutions examined were at approximately the same pH, the variation is not likely to be large). Spectra were measured on 5—10% w/w solutions in D_2O, the aminopropanols being converted into salts by addition of trifluoroacetic acid. Since J and δ values could not be obtained from the spectra, the " chemical shifts " quoted in the text refer to the approximate centre of gravity of complex bands.

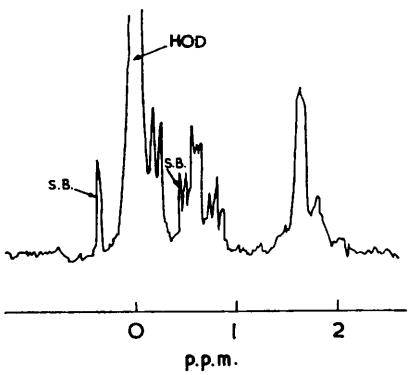
When streptolidine dihydrochloride was dissolved in heavy water the exchangeable protons were largely replaced by deuterium and the spectrum of this solution (Figure) represented only the five protons attached to carbon. Comparison with the previous poorly resolved spectrum in deuterotrifluoroacetic acid showed that there was no absorption to low field of the HOD peak (about 5·3 τ) and that this peak did not conceal any of the spectrum. The appearance of a doublet at lowest field had previously been associated with the methylene group of (III) rather than (IV), but since the spectrum has two other groups of about equal intensity the doublet must arise from only one proton. Comparison with the spectra of acidified (CF_3·CO_2H) heavy water solutions of 1-aminopropan-2-ol and 2-aminopropan-1-ol shows that no absorptions are to be expected at such low field from either grouping (III) or (IV). The only other proton that would be expected to give rise to a simple doublet in the deuterated salt (V) is that at position 5. The absorption is at rather low field (about 5·5 τ) and indicates a marked deshielding effect by the protonated guanidino-group.

The spectra of the deuterated amino-propanol salts can be interpreted as ABC [7] systems in

[1] Johnson and Westley, *J.*, 1962, 1642.
[2] van Tamelen, Dyer, Whaley, Carter, and Whitfield, *J. Amer. Chem. Soc.*, 1961, **83**, 4295.
[3] Carter, Clark, Kohn, Rothrock, Taylor, West, Whitfield, and Jackson, *J. Amer. Chem. Soc.*, 1954, **76**, 566.
[4] Brockmann and Musso, *Chem. Ber.*, 1955, **88**, 648.
[5] Nakanishi, Ito, and Hirata, *J. Amer. Chem. Soc.*, 1954, **76**, 2845.
[6] Carter, Sweeley, Daniels, McNary, Schaffner, West, van Tamelen, Dyer, and Whaley, *J. Amer. Chem. Soc.*, 1961. **83**, 4296.
[7] Pople, *Mol. Phys.*, 1958, **1**, 3.

which the A proton signals are split into 1 : 3 : 3 : 1 quartets by the adjacent methyl groups. In the spectrum of 1-aminopropan-2-ol the $>CH_2$ group gives a complex signal with a strong peak at 2·05 p.p.m. and two smaller absorptions at slightly higher field, the $>CH$ group gives a complex signal of at least twelve lines at 1·03 p.p.m., and the methyl group a doublet (J 6·4 c./sec.) at 3·72 p.p.m. In the spectrum of 2-aminopropan-1-ol the methyl group appears as a doublet (J 6·1 c./sec.) at 3·94 p.p.m. and the remainder of the absorptions as a very complex group at about 1·65 p.p.m.

On the basis of the two model systems it is possible to give a qualitative account of the streptolidine spectrum (Figure). The appearance of two groups of absorptions of about equal intensities (0·57 and 1·63 p.p.m.) strongly favours structure (I) for the base, as the spectrum of 2-aminopropan-1-ol requires that at least 3 protons should give a close group of absorptions if



Nuclear magnetic resonance spectrum of streptolidine dihydrochloride in deuterium oxide.

the isomeric side-chain (as in II) is present. Further evidence is the similarity of the 1·63 p.p.m. group in the Figure to the amino-methylene absorption of 1-aminopropan-2-ol. Thus, although the nuclear magnetic resonance spectra cannot be interpreted completely, structure (I) rather than (II) is now favoured for streptolidine on the basis of them. The same modification of the side-chain will be necessary in the structure of the antibiotic, although this may be incorporated as a β-lactam involving the adjacent carboxyl group.[2]

We gratefully acknowledge the award of a Commonwealth United Kingdom Postgraduate Fellowship to J. H. B.

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806. *The Density, Viscosity, and Surface Tension of Vanadium Pentafluoride.*

By R. G. CAVELL and H. C. CLARK.

BOTH the high specific conductivity and the Trouton constant [1,2] suggest that vanadium pentafluoride is associated, and also that it ionises:

$$2VF_5 \rightleftharpoons VF_4^+ + VF_6^-$$

Intermolecular association in covalent fluorides seems to occur through fluorine-bridge bond formation; thus the ^{19}F nuclear magnetic resonance spectrum of antimony pentafluoride indicates the formation of polymeric chains through such fluorine-bridge bonds.[3] The extent of intermolecular association in a liquid appears to be reflected by properties such as surface tension and viscosity, and these have now been determined for liquid vanadium pentafluoride.

[1] Clark and Emeléus, *J.*, 1957, 2119.
[2] Trevorrow, Fischer, and Steunenberg, *J. Amer. Chem. Soc.*, 1957, **79**, 5165.
[3] Hoffman, Holder, and Jolly, *J. Phys. Chem.*, 1958, **62**, 364.

Experimental.—Vanadium pentafluoride was prepared by the direct fluorination of powdered vanadium metal as previously described.[1]

Density. A silica dilatometer, calibrated with mercury, was filled *in vacuo* with vanadium pentafluoride and sealed. The volume of liquid was determined at approximately 5° intervals over the temperature range 20—45°, with both increasing and decreasing temperature to check the reproducibility; the results of two experiments are shown in the following Table:

t (°c)	20·0	25·2	30·2	34·7	39·8	44·9	30·1	24·3	20·4	26·6
ρ (g. c.c.$^{-1}$)	2·508	2·489	2·478	2·457	2·435	2·414	2·470	2·489	2·500	2·482
t (°c)	20·6	25·3	30·9	35·1	40·4	45·0	37·7	30·3	25·0	20·2
ρ (g. c.c.$^{-1}$)	2·491	2·474	2·459	2·444	2·424	2·406	2·435	2·462	2·479	2·494

The average expression for the density from two experiments, including standard deviations, is $\rho = 2{\cdot}483\ (\pm 0{\cdot}004) - 0{\cdot}00349(t - 25°)\ (\pm 0{\cdot}00008)$ g. c.c.$^{-1}$, and the average coefficient of expansion is $\alpha = 1{\cdot}475\ (\pm 0{\cdot}025) \times 10^{-3}$ deg.$^{-1}$.

Viscosity. A Pyrex viscometer was used, consisting of a 15 cm. length of 1 mm. capillary tubing joining an upper bulb of about 1 c.c. capacity to a lower bulb of about 2 c.c. capacity. An 8 mm. diameter tube, parallel to the capillary, was joined to the top of the large reservoir and was fitted at the top with a metal tap (Hoke type 431). A second tap provided a connection between the two arms of the viscometer and these permitted a variation in the relative pressure between the arms. After the apparatus had been " baked " *in vacuo* at 100° for two days, approximately 2 c.c. of vanadium pentafluoride was distilled in. The viscometer was then sealed to a vacuum line through which a variable pressure of dry nitrogen could be provided. With the tap connecting the two arms of the viscometer closed, the application of nitrogen through the main tap forced the liquid into the upper reservoir. The pressure between the two arms was then equalised and, with the viscometer immersed in a thermostated water-bath, the liquid was allowed to flow under the influence of its hydrostatic pressure into the lower reservoir. Where possible, several measurements of the flow time at each temperature were made. Considerable difficulty was caused by the volatility of vanadium pentafluoride, which seriously limited the accessible temperature range and also caused some of the pentafluoride to distil out of the viscometer when the pressure of nitrogen was reduced between measurements. The latter step was necessary in order to avoid using increasingly greater pressures of nitrogen. Despite extreme precautions, some decomposition of the pentafluoride occurred, as shown by a gradual darkening of the liquid during the experiment. The viscometer was calibrated with concentrated sulphuric acid, this being the only liquid of reliably known viscosity which has a density and viscosity comparable with that of vanadium pentafluoride. The results are shown in the following Table. The number of determinations at each temperature is given in brackets beside the average value of the viscosity.

t (°c)	25·35	25·45	31·9	32·0	27·3	27·3
η (centipoise)	124·2 (3)	125·7 (2)	86·8 (1)	76·4 (3)	110·4 (1)	120·0 (1)

From eleven measurements of flow time, at temperatures in the range 25·35—32·00°, the viscosity of vanadium pentafluoride can be expressed by the equation $\eta = 124 - 7{\cdot}2(t - 25°)$ centipoise. Considering the above sources of error, the viscosity given by this equation probably has a maximum error of $\pm 20\%$.

Surface Tension. In one experiment, (i), the capillary rise in three capillaries ranging from 0·5—1·5 mm. internal diameter was measured and in another experiment, (ii), a differential capillary tensiometer [4] was used. The surface tension, γ, was calculated from the expression $\gamma = f\Delta h/\rho$, where f = apparatus factor, Δh = difference in level of liquid in each of two capillaries (or the height of liquid in the capillary above the level in the reservoir), and ρ = density of the liquid. The apparatus factor, f, was determined for each apparatus by measuring Δh for a liquid of known density and surface tension, such as water or benzene. Measurements were made over the temperature range 24·5—37·0°; the results for the two experiments are shown in the following Table.

		(i)			(ii)	
t (°c)	24·5	29·7		34·8	29·5	37·0
γ (dynes cm.$^{-1}$)	18·35	18·0	17·75	16·75	17·15	16·5

[4] Dodd and Robinson, " Experimental Inorganic Chemistry," Elsevier, Amsterdam, 1957, Fig. 156 a.

Least-squares analysis of the data for both experiments gives for the surface tension of vanadium pentafluoride, $\gamma = 18{\cdot}2 - 0{\cdot}142(t - 25°)$ dynes cm.$^{-1}$, with a probable error of $\pm 0{\cdot}2$ and a standard deviation of $\pm 0{\cdot}3$.

Discussion.—Ruff and Lickfett [5] reported the density of solid vanadium pentafluoride as being 2·1766 g. c.c.$^{-1}$ at 19°. This is clearly in error, since liquid vanadium pentafluoride has a higher density, and a very marked contraction occurred when the liquid was frozen in the dilatometer. Ruff and Lickfett's erroneous result was probably due to extensive hydrolysis of their samples of the pentafluoride to the oxytrifluoride. The present value for the density of liquid vanadium pentafluoride at 25°, 2·483 g. c.c.$^{-1}$, is comparable with the densities [6] of antimony pentafluoride (2·99 g. c.c.$^{-1}$), bromine trifluoride (2·80 g. c.c.$^{-1}$), bromine pentafluoride (2·46 g. c.c.$^{-1}$), and iodine pentafluoride (3·19 g. c.c.$^{-1}$).

Although the equation obtained is not exceptionally accurate, the viscosity of vanadium pentafluoride is clearly much higher than for most liquid fluorides. Thus, for bromine trifluoride the viscosity at 25° is 2·22 centipoise, and for iodine pentafluoride 2·19 centipoise.[6] Only antimony pentafluoride, with a viscosity of 460 centipoise [7] at 25°, has a higher viscosity than vanadium pentafluoride, and it has been shown [3] that the former is associated, being in the form of fluorine-bridged polymers. The high viscosity of vanadium pentafluoride thus indicates considerable polymeric association in the liquid.

The value of 18·2 dynes cm.$^{-1}$ for the surface tension of vanadium pentafluoride at 25° is lower than the values for all associated fluorides.[6] This is surprising, since in the associated fluorides viscosity and surface tension decrease in the same order: $SbF_5 > BrF_3 > IF_5 > BrF_5 > ClF_3$. While the viscosity of vanadium pentafluoride falls between those of antimony pentafluoride and bromine trifluoride, the surface tension is less than that of chlorine trifluoride. The high viscosity of vanadium pentafluoride may have led to a false result for the surface tension, since for antimony pentafluoride reliable values for the surface tension could not be obtained by capillary rise methods [8] and the maximum bubble-pressure method had to be used. If this were so for vanadium pentafluoride, then it is surprising that two different capillary rise methods should give results in such good agreement.

The molar surface energy, Γ, given by the equation $\Gamma = \gamma(Mv)^{2/3}$ where γ is the surface tension, M is the molecular weight, and v is the specific volume, was calculated for vanadium pentafluoride and plotted against temperature. The Eötvos coefficient, $(d\Gamma/dt)$, was found to be $-1{\cdot}9$, as compared with the value of $-2{\cdot}1$ expected for non-associated liquids. The ratio of these two values indicates that the degree of molecular association is apparently not much greater than unity. However, many associated, as well as non-associated, liquids yield the non-associated value for the Eötvos coefficient and thus little reliable information can be deduced from this coefficient concerning the degree of molecular association. The high viscosity of vanadium pentafluoride, which is a more reliable indication of association, means that the liquid is probably highly associated in spite of the low surface tension and normal Eötvos coefficient. The similarity of the viscosity to that of antimony pentafluoride, both of which are much more viscous than the halogen fluorides, suggests that both pentafluorides are associated, being in the form of chain polymers, in contrast to the dimeric species probably present in the halogen fluorides.

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Department of Chemistry, University of British Columbia,
Vancouver 8, B.C., Canada. [*Received, January 14th*, 1963.]

[5] Ruff and Lickfett, *Ber.*, 1911, **44**, 2539.
[6] Clark, *Chem. Rev.*, 1958, **58**, 869.
[7] Woolf and Greenwood, *J.*, 1950, 2200.
[8] Hub and Robinson, *J.*, 1954, 2640.

807. *The Chemical Synthesis of Polysaccharides. Part IV.*[1] *Synthesis of* 6-O-α-D-*Glucopyranosyl*-D-*galactose.*

By I. J. Goldstein and W. J. Whelan.

In the attempt to synthesize 6-*O*-α-D-glucopyranosyl-D-galactose by the Koenigs–Knorr reaction,[2] the usual condensing agent for the formation of β-linked oligosaccharides, silver carbonate, was replaced by mercuric cyanide. The latter salt had been used by Matsuda and Sekiguchi[3] in the similar synthesis of a glucobiose, an α-linkage being created (nigerose, α-1,3-glucobiose). However, the reaction between 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide and 1,2:3,4-di-*O*-isopropylidene-D-galactose in presence of mercuric cyanide led exclusively to formation of a β-1,6-glycosidic bond. The desired product was, however, obtained by applying Lindberg's anomerization reaction[4] to 6-*O*-β-glucosylgalactose octa-acetate. After establishment of equilibrium between the α- and β-1,6-bonded disaccharides, the latter was removed by hydrolysis of the free sugar with β-glucosidase.

The structure of the 6-*O*-glucosylgalactose was established as follows. On reduction to the alcohol, followed by acid hydrolysis, the reducing sugar set free was glucose, characterized as the phenylosazone. When the disaccharide alcohol was oxidized with sodium metaperiodate under conditions selective for the galactitol component,[5] the consumption of periodate was 3·96 mol., and 1·1 mol. of formaldehyde were released. The calculated values for 6-*O*-α-glucosylgalactose are 4 and 1 mol., respectively. This evidence, taken with the structures of the substances used in the synthesis and the optical rotation of the disaccharide ($[\alpha]_D$ +125° in water), defines the sugar as 6-*O*-α-D-glucopyranosyl-D-galactose. No crystalline characterizing derivative could be obtained.

The synthesis of this disaccharide has not previously been described, but Stocker, Staub, Tinelli, and Kopacka[6] recently obtained a glucosylgalactose by partial hydrolysis of polysaccharides from *Salmonella senftenberg* and *S. typhimurium*. This sugar was believed to contain either a 1,3- or a 1,6-linkage. It behaved in the same way as our disaccharide in paper chromatography and electrophoresis, and the two sugars were tested as inhibitors of precipitation in the reaction between *S. senftenberg* polysaccharide and antiserum of *S. typhimurium*. The degrees of inhibition caused by 2 and 10 μmoles of the two sugars were 37% and 68%, respectively, for the bacterial disaccharide, and 41% and 70% for the synthetic disaccharide. It may be concluded that the two sugars are identical.[7] We thank Dr. A. M. Staub for providing these previously unpublished results.

Experimental.—General methods. Evaporations were carried out at 45° under reduced pressure. Paper chromatograms were irrigated with the butanone–water azeotrope (solvent *A*) or ethyl acetate–pyridine–water (10 : 4 : 3 v/v) (solvent *B*). Paper electrophoresis was conducted in borate buffer (pH 10). Spray reagents for sugars separated on paper were silver nitrate–sodium hydroxide[8] or aniline–diphenylamine–phosphoric acid.[9]

Synthesis of 6-O-β-D-*glucopyranosyl*-D-*galactose.*[3] 2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl bromide (8·2 g.) and 1,2:3,4-di-*O*-isopropylidene-D-galactose (5·3 g.) in dry nitromethane (60 ml.) with finely powdered mercuric cyanide (8·5 g.) were shaken overnight and then heated under reflux on a boiling-water bath for 8 hr. The product was freed from salts[3] and deacetylated.[10] Paper chromatography in solvent *A* showed glucose and a non-reducing substance having R_F 0·60. The syrup was passed through a "Chromax" cellulose column

[1] Part III, *J.*, 1962, 4232.
[2] Evans, Reynolds, and Talley, *Adv. Carbohydrate Chem.*, 1951, **6**, 27.
[3] Matsuda and Sekiguchi, *Nippon Nagei-kagaku Kaishi*, 1959, **33**, 309.
[4] Lindberg, *Acta Chem. Scand.*, 1949, **3**, 1355.
[5] Clancy and Whelan, *Chem. and Ind.*, 1959, 673.
[6] Stocker, Staub, Tinelli, and Kopacka, *Ann. Inst. Pasteur*, 1960, **98**, 505.
[7] Staub, *Pathologia et Microbiologica*, 1961, **24**, 890.
[8] Trevelyan, Procter, and Harrison, *Nature*, 1950, **166**, 444.
[9] Buchan and Savage, *Analyst*, 1952, **77**, 401.
[10] Zemplen, *Ber.*, 1926, **59**, 1258.

(LKB Produkter, Sweden; 40 × 4 cm.) irrigated with solvent *A*, and the substance having R_F 0·60 was collected in the first 2 l. of effluent; on evaporation the residue weighed 3·3 g.

The syrup was heated in 0·1N-sulphuric acid (50 ml.) at 70° for 2 hr., then neutralized with barium carbonate. The product (2·3 g.) on paper chromatography in solvent *B* showed glucose, a reducing disaccharide, and starting material. The mixture was resolved on a charcoal–Celite column (250 g., 1 : 1) by elution with water (2 l.) to remove the monosaccharide, and with 6% aqueous ethanol (2 l.) to remove the disaccharide. The ethanolic eluate was treated with Biodeminrolit ion-exchange resin (Permutit Co. Ltd.) in the carbonate form,[11] and evaporated to a syrup (1·5 g.) having $[\alpha]_D$ +10° in water (*c* 1). Freudenberg *et al.*[12] give $[\alpha]_D$ +13·9° for 6-*O*-β-D-glucopyranosyl-D-galactose. The disaccharide was acetylated with sodium acetate–acetic anhydride to give a syrupy acetate (2·0 g.) having $[\alpha]_D$ +1° in chloroform (*c* 1).

Anomerization of 6-O-β-D-*glucopyranosyl*-D-*galactose*.[4] The acetate (2·0 g.) in dry chloroform (25 ml.) was mixed with titanium tetrachloride (2·5 g.) in the same solvent (25 ml.). Treatment as by Lindberg [4] yielded a mixture of sugar acetates (1·7 g.). These were deacetylated [10] to a mixture (0·80 g.) of glucose, galactose, and a component with the mobility of a disaccharide ($R_{glucose}$ 0·35) (solvent *A*).

Enzymic hydrolysis of 6-O-β-D-*glucopyranosyl*-D-*galactose and isolation of* 6-O-α-D-*glucopyranosyl*-D-*galactose*. The sugar mixture (0·76 g.) in water (39 ml.) was adjusted to pH 5·0. An aqueous solution of almond emulsin [13] (39 ml., 0·78 g.) was added and the mixture again adjusted to pH 5·0. The digest was incubated under toluene at 35° with a sugar-free control. The reducing power [14] (as glucose) rose from 260 mg. to 435, 445, and 460 mg. at 21, 42, and 64 hr., respectively. The enzyme was inactivated by heat and the digest de-ionized. The mixture of mono- and di-saccharides was resolved on sheets of Whatman No. 3MM paper (solvent *B*), and the disaccharide (0·25 g.) was obtained, having $[\alpha]_D$ +116° in water (*c* 1). A sample (5 mg.) was treated with emulsin as before for 48 hr. and small amounts of glucose and galactose were formed. The entire disaccharide mixture was therefore re-treated with emulsin, and the disaccharide component worked up as before, to yield syrupy 6-*O*-α-glucosyl-D-galactose (0·15 g.), $[\alpha]_D$ +125° in water (*c* 1), M_G [15] 0·61 (M_G of nigerose, 0·61).

Characterization of 6-O-α-D-*glucopyranosyl*-D-*galactose*. A solution of the disaccharide was treated with sodium borohydride, and the disaccharide alcohol was hydrolysed with acid for 6 hr. to determine its concentration (2·33 mg./ml.) in terms of the glucose set free.[16] From a portion of the hydrolysate phenylglucosazone was obtained, having m. p. and mixed m. p. 205°. Glucose and galactitol were detected by chromatography of the hydrolysate (solvent *B*).

The disaccharide alcohol (2 ml., 4·66 mg.) was brought to pH 5·0 and 0·02M-sodium metaperiodate (4 ml.) and water were added to 200 ml. At intervals portions (20 ml.) were withdrawn, added to a mixture of 2·5% potassium iodide (10 ml.) and 3N-sulphuric acid (2 ml.) and titrated with 0·01N-sodium thiosulphate, to determine the consumption of periodate. Formaldehyde was estimated with chromotropic acid as by Parrish and Whelan [17] on 1·5 ml. portions of the digest. The results were as follows:

Time (min.)	10	20	30	60	180	360
Periodate consumed (mol.)	2·92	3·34	3·60	3·70	3·70	3·96
Formaldehyde (mol.)	0·86	1·01	1·06	1·10	1·10	1·10

Acetylation (sodium acetate–acetic anhydride), benzoylation (benzoyl chloride–pyridine), and *p*-nitrobenzoylation of the sugar failed to yield crystalline esters.

We are grateful to the John Simon Guggenheim Memorial Foundation for the award of a fellowship (to I. J. G.) and thank Imperial Chemical Industries Limited for the loan of the Chromax column.

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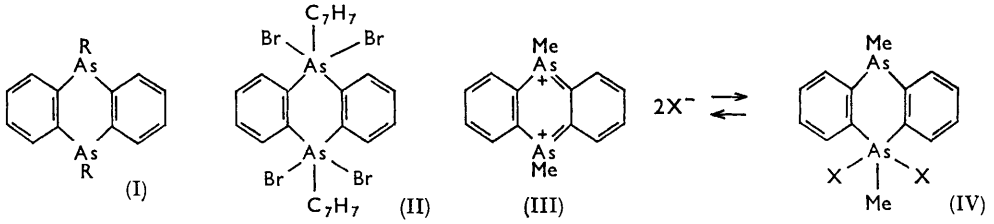
[*Received, January 18th*, 1963.]

[11] Woolf, *Nature*, 1953, **171**, 841.
[12] Freudenberg, Wolf, Knopf, and Zaheer, *Ber.*, 1928, **61**, 1743.
[13] Tauber, *J. Biol. Chem.*, 1932, **99**, 259.
[14] Shaffer and Hartmann, *J. Biol. Chem.*, 1921, **45**, 365.
[15] Foster, *J.*, 1953, 983.
[16] Pirt and Whelan, *J. Sci. Food Agric.*, 1951, **2**, 224.
[17] Parrish and Whelan, *Stärke*, 1961, **13**, 231.

808. *Cyclic Diarsines. Part VIII.*[1] *A Novel Type of Tautomerism Shown by 5,10-Dihydro-5,10-dimethylarsanthren Di-iodide.*

By Frederick G. Mann.

Consideration of recent work shows that the 5,10-dihydroarsanthren ring system (as in I) can adopt various configurations according to the nature of the attached groups. The 3-covalent arsenic atom has an intervalency angle of *ca.* 98° in simple symmetric arsines, for example, $AsCl_3$ 98·4° ± 0·5°,[2] $AsBr_3$ 100° ± 2°,[3] AsI_3 98·5°,[4] $AsMe_3$ 96° ± 5°.[5] If this angle is retained in a 5,10-disubstituted 5,10-dihydroarsanthren (I; R = alkyl or aryl), the molecule must be folded about the As–As axis, the two *o*-phenylene groups subtending at this axis a (calculated) angle of 121°. Further, such a compound should exist in two geometric forms, the *cis*-form having both substituents within this angle and the *trans*-form having one substituent within and the other outside this angle. Both forms of the 5,10-di-*p*-tolyl derivative (I; R = C_6H_4Me) have been isolated.[6] Both forms gave the same tetrabromide (II), which was readily converted into a dibromide, whose properties indicated an ionic structure (as III; X = Br).



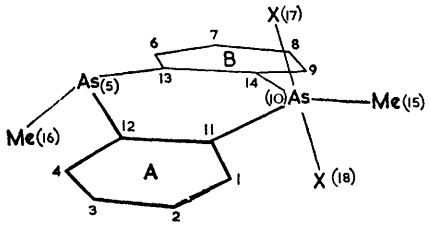
A more detailed examination of the colourless 5,10-dimethyl analogue (III; X = Br) confirmed its ionic structure in solution:[7] for example, the dibromide when treated in cold ethanolic solution with ethanolic sodium iodide or picrate rapidly deposited the di-iodide (III; X = I) and dipicrate (III; X = $C_6H_2N_3O_7$), respectively. The di-iodide, however, formed deep orange crystals, which gave pale yellow methanolic and ethanolic solutions: the addition of ethanolic sodium picrate to these solutions again rapidly deposited the dipicrate. It was, therefore, suggested that the crystalline di-iodide had the covalent structure (IV; X = I) and that in solution it formed an equilibrium mixture of this compound and the salt (III; X = I).

This attribution of tautomerism to the di-iodide rested solely on the retention in solution of the colour of the crystalline material. This dark orange colour is characteristic of simple aryl tertiary-arsine di-iodides, for example, $MePh_2AsI_2$ (deep orange), Ph_3AsI_2 (yellow-orange),[8] $(p\text{-}Me\cdot C_6H_4)_3AsI_2$ (reddish-yellow).[9] The dibromide (IV; X = Br), being colourless in the solid state and in solution, affords on this basis no evidence of tautomerism. The absence of colour is to be expected, for simple tertiary arsine dibromides, such as $Et_2PhAsBr_2$,[10] $MePh_2AsBr_2$, Ph_3AsBr_2,[8,9] $(p\text{-}C_6H_4Me)_3AsBr_2$[9] are colourless, and a pale yellow colour appears only in more complex examples such as $(2,4,5\text{-}C_6H_2Me_3)_3AsBr_2$.[9] Furthermore, the cation in (III), which, having a resonance system similar to that of anthracene, is almost certainly planar, must also be colourless, as it is undoubtedly present in solutions of the dibromide (III; X = Br).

[1] Part VII, Forbes, Mann, Millar, and Moelwyn-Hughes, *J.*, 1963, 2833.
[2] Kisliuk and Townes, *J. Chem. Phys.*, 1950, **18**, 828.
[3] Lister and Sutton, *Trans. Faraday Soc.*, 1941, **37**, 393.
[4] Finbak and Hassel, *Arch. Math. Naturv.*, 1941, **44**, *B*, 3; Hassell and Viervoll, *Acta Chem. Scand.*, 1947, **1**, 149.
[5] Springall and Brockway, *J. Amer. Chem. Soc.*, 1938, **60**, 996.
[6] Chatt and Mann, *J.*, 1940, 1184.
[7] Emrys R. H. Jones and Mann, *J.*, 1955, 411,
[8] Steinkopf and Schwen, *Ber.*, 1921, **54**, 1437.
[9] Michaelis, *Annalen*, 1902, **321**, 141.
[10] Winmill, *J.*, 1912, **101**, 718.

More decisive evidence for this unique type of tautomerism was clearly required, and an *X*-ray crystal structure analysis of our dibromide and di-iodide was kindly undertaken by Dr. D. June Sutor and Miss Frances R. Harper. Their structure results alone have been recorded; [11] a discussion of the chemical significance of these results was omitted, for inclusion in the present series of papers.

Their results show that the dibromide and di-iodide have virtually identical structures corresponding to the covalent form (IV): this evidence, combined with that outlined above, leaves no doubt that the di-iodide in solution does exist as a tautomeric equilibrium of the forms (III) and (IV). There is at present however no decisive evidence for the existence in solution of the covalent dibromide (IV; X = Br).



Diagrammatic structure of the compounds (IV; X = Br or I), the normal numbering of the arsanthren ring being extended as shown. The As(5) and As(10) atoms are depicted in a horizontal line in the plane of the paper, with both of the *o*-phenylene groups directed slightly downwards, the group (A) towards and the other (B) away from the observer. Me(15) and Me(16), and the two halogen atoms X attached to the atoms As(10), are in the plane of the paper.

Certain other features of the structure of the crystalline dibromide and di-iodide deserve mention. It is known that the crystalline trimethylstibine dichloride, dibromide, and di-iodide, $[Me_3SbX_2]$, have a trigonal-bipyramid structure, the methyl groups and the antimony atom being therefore in one plane with a central intervalency angle of 120°.[12] In the dimethylarsanthren dibromide (see Figure) there is strong evidence that the As(10) atom is similarly in the same plane as the three carbon atoms to which it is linked, and that the Br(17)–As(10)–Br(18) atoms are almost linear. This trigonal bipyramid configuration of the As(10) atom if undistorted would tend to make the tricyclic system planar, but the As(5) atom still retains its pyramidal configuration; consequently although the molecule is still folded about the As–As axis, the angle subtended by the two *o*-phenylene groups at this axis is now increased to *ca.* 157°. The Br(18) and Br(17) atoms, *i.e.*, the atoms within and outside this angle, respectively, are tilted as shown at 14° from the perpendicular to the As–As axis, presumably to accommodate the folded structure: moreover, the closer proximity of the *o*-phenylene groups also increases slightly but significantly the arsenic–halogen distance within the angle, the values being As–Br(18) 2·66, As–Br(17) 2·59, As–I(18) 2·98, and As–I(17) 2·80 Å. These distances are longer than those in normal covalent compounds, for example, As–Br, 2·35 in $AsBr_3$ and Me_2AsBr; [3,13] As–I, 2·53 in AsI_3 and Me_2AsI.[13,14] This is to be expected, for in the trimethylstibine dihalides, Me_3SbX_2, the two Sb–X distances in each compound are of course equal but are longer than the normal covalent distances.

In view of the structure of the two compounds (IV), there can be little doubt that both arsenic atoms have the trigonal-bipyramid configuration in the tetrabromoarsanthren derivatives of type (II) and in the corresponding tetrahydroxides; consequently the tricyclic system and the organic groups linked to the arsenic atoms can be regarded as being in one horizontal plane, with the bromine (or hydroxyl) groups placed vertically above and below the arsenic atoms. The tricyclic arsanthren system can therefore have the folded structures (I) and (IV) and also almost certainly two planar structures (II) and (III).

The properties of the structurally similar orange 5,5′-10,10′-bis-*o*-xylylenebisarsanthronium tetra-iodide indicate that this salt also forms a similar equilibrium in solution, but it has been only briefly investigated.[7]

[11] Sutor and Harper, *Acta Cryst.*, 1959, **12**, 585.
[12] Wells, *Z. Krist.*, 1938, **99**, 367.
[13] Skinner and Sutton, *Trans. Faraday Soc.*, 1944, **40**, 164.
[14] Hassell and Viervoll, ref. 4.

Note Added in Proof.—Mislow, Zimmerman, and Mellilo (*J. Amer. Chem. Soc.*, 1963, **85**, 594) have recently asserted, solely on the basis of theoretical considerations, that tricyclic systems of type (I), having hetero-atoms in positions 5 and 10, are unlikely to be "stably folded" because they can flex so readily about the planar position. In addition to the above experimental evidence, the *X*-ray crystal structure analysis of other compounds of this type is now being undertaken.

Experimental.—Methyldiphenylarsine dibromide and di-iodide ($MePh_2AsX_2$; X = Br or I). These compounds were prepared to record their colour, for they are the closest simple aryl analogues of the compounds (IV; X = Br or I). Methyldiphenylarsine, prepared by the action of methylmagnesium iodide on diphenylarsenous chloride, Ph_2AsCl, had b. p. 165—167°/15 mm. (lit.,[15] 163—170°/15 mm.). A solution of dry bromine in light petroleum (b. p. 40—60°) was added dropwise with stirring to the arsine, also dissolved in the petroleum, until the mixture acquired a persistent very pale yellow colour. The pale cream-coloured *dibromide* which had meanwhile separated was rapidly collected, washed with petroleum, and dried in a vacuum-desiccator over paraffin wax shavings; it had m. p. 102—104° (effervescence) (Found: C, 38·75; H, 3·0. $C_{11}H_{13}AsBr_2$ requires C, 38·6; H, 3·2%).

A chloroform solution of the arsine was added with shaking to a similar solution of iodine until a clear deep orange solution was obtained. Evaporation in a desiccator gave a dark oil which solidified when vigorously stirred with the petroleum, giving the *di-iodide* as a deep orange crystalline powder, m. p. 95—96°, after collection, washing with petroleum, and drying as before (Found: C, 31·3; H, 2·6. $C_{13}H_{13}AsI_2$ requires C, 31·3; H, 2·6%).

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, January 26th*, 1963.]

[15] Burrows and Turner, *J.*, 1920, **117**, 1381; 1921, **119**, 430.

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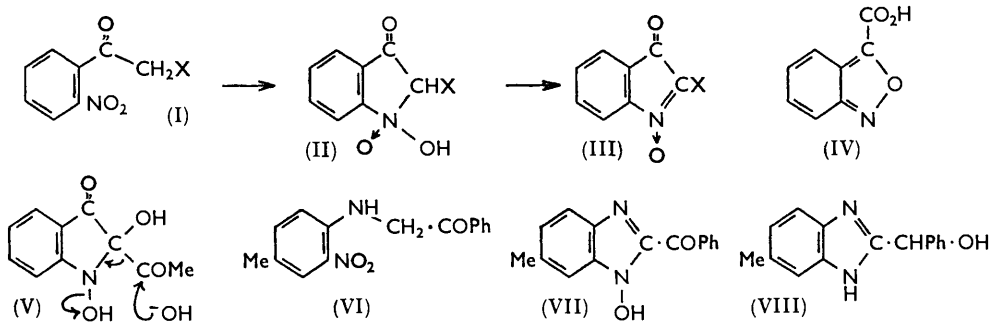
809. *Substituent Interactions in* ortho-*Substituted Nitrobenzenes. Part V.*[1]

By J. D. LOUDON and G. TENNANT.

WE record three examples of base-catalysed interaction, which, despite diversity in the types of product isolated, may all be initiated by nucleophilic attack on the nitro-group by the side chain, *e.g.*, (I) ⟶ (II).



2-Nitrophenacyl chloride (I; X = Cl), heated with aqueous potassium hydroxide, afforded anthranil-3-carboxylic acid (IV). It is suggested that the reaction proceeds through formation, and known rearrangement,[2] of 1-hydroxyisatin (= 2-hydroxyisatogen; cf. III, X = OH). Similar treatment of *o*-nitrobenzoylacetone (I; X = Ac) gave isatin which is probably derived by hydroxide attack on the hydrated form (V) of the isatogen

[1] Part IV, *J.*, 1962, 3092.
[2] Arndt, Eistert, and Partale, *Ber.*, 1927, **60**, 1364.

(III; X = Ac). 2-Nitro-*N*-phenacyl-*p*-toluidine (VI) reacted with alkali to give, together with unidentified material, 2-benzoyl-1-hydroxy-6-methylbenzimidazole (VII). The structure of this product was proved by hydrogenolysis of its *O*-acetate to the alcohol (VIII) which was identical with a specimen synthesised [3] from mandelic acid and 4-methyl-*o*-phenylenediamine.

Experimental.—Anthranil-3-carboxylic acid. 2-Nitrophenacyl chloride (0·1 g.) was warmed with N-sodium hydroxide (0·5 ml.) until dissolution was complete (10 min.) and then for 5 min. further, before the red solution was cooled and acidified. The resultant precipitate afforded anthranil-3-carboxylic acid (0·06 g.), identified by m. p. and mixed m. p. 191—192° (from hot water) and by its infrared spectrum.

Isatin. A suspension of *o*-nitrobenzoylacetone (0·2 g.) in ethanol (2 ml.), mixed with a solution of potassium hydroxide (0·2 g.) in water (2 ml.), was heated under reflux for ½ hr. The red solution was concentrated *in vacuo*, clarified by filtration, and acidified, affording isatin, m. p. and mixed m. p. 205° (Found: C, 65·6; H, 3·7; N, 9·3. Calc. for $C_8H_5NO_2$: C, 65·3; H, 3·5; N, 9·5%).

2-Benzoyl-1-hydroxy-6-methylbenzimidazole. A 20% aqueous solution (2 ml.) of potassium hydroxide was added dropwise to a suspension of 2-nitro-*N*-phenacyl-*p*-toluidine (1 g.) in boiling ethanol (15 ml.). A vigorous reaction occurred and, after heating had been continued for 2 hr., the solvent was removed *in vacuo* and the residue treated with water. Extraction with ether gave some benzoic acid, removed by washing the ethereal extract with aqueous sodium hydrogen carbonate, whereafter evaporation of the resultant, dried ethereal solution afforded the *benzimidazole* (VII). This crystallised from methanol in a solvated *form*, m. p. 82—84° (Found: C, 67·4; H, 5·8; N, 10·1. $C_{15}H_{12}N_2O_2,CH_4O$ requires C, 67·6; H, 5·6; N, 9·9%), changing, on being powdered and heated at 70° *in vacuo*, to the unsolvated *form*, m. p. 132° (Found: C, 71·7; H, 4·9; N, 11·2. $C_{15}H_{12}N_2O_2$ requires C, 71·4; H, 4·8; N, 11·1%). Heated with acetic anhydride, it gave the *1-acetoxy-compound*, m. p. 134° (from methanol) (Found: C, 69·1; H, 4·5; N, 9·7. $C_{17}H_{14}N_2O_3$ requires C, 69·4; H, 48; N, 9·5%). This was hydrogenated in ethanol over 5% palladium–charcoal, affording 2-α-hydroxybenzyl-5-methylbenzimidazole which was identified by m. p. and mixed m. p. 205—207° (lit.,[3] m. p. 199—201°) and by its infrared spectum (Found: C, 75·8; H, 5·7; N, 11·9. Calc. for $C_{15}H_{14}N_2O$: C, 75·6; H, 5·9; N, 11·8%).

THE UNIVERSITY, GLASGOW, W.2. [*Received, February 15th*, 1963.]

[3] Bistrzycki and Przeworski, *Ber.*, 1912, **45**, 3483.

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810. 1-(*Pyridyl*)*alkan*-1-*ols*.

By N. P. BUU-HOÏ, P. JACQUIGNON, A. ROSE, J. F. SABATHIER, and M. P. SINH.

MANY alcohols in the pyridyl series have already been investigated, but most of them are either primary alcohols,[1] or secondary alcohols with their hydroxy-group remote from the heterocyclic nucleus.[2] In a general investigation on relations between chemical structure and choleretic activity,[3] we have prepared a large number of 1-(pyridyl)alkan-1-ols in view of their analogy with the strongly choleretic 1-arylalkan-1-ols.[4] The intermediates were the three (commercial) pyridine aldehydes, which underwent Grignard reactions with primary alkylmagnesium halides. These alcohols were liquids, except for the higher analogues, and their choleretic effect in rats was optimal in the case of 1-3′-pyridylbutan-1-ol; the 2-pyridyl and 4-pyridyl series were notably more toxic.[5] Chemically,

[1] Cf. Harries and Lenart, *Annalen*, 1915, **410**, 95; Dehnel, *Ber.*, 1900, **33**, 3498; Löffler and Stietzel, *Ber.*, 1909, **42**, 124.

[2] Cf. Hunt and Fosbinder, *J. Amer. Chem. Soc.*, 1941, **63**, 2771; Meisenheimer and Mahler, *Annalen*, 1928, **462**, 308.

[3] Buu-Hoï and Xuong, *Compt. rend.*, 1959, **249**, 970; Buu-Hoï, Xuong, and Diep, *J. Org. Chem.*, 1961, **26**, 1673.

[4] See Dallacker, Pauling-Walther, and Lipp, *Arzneimittelforsch.*, 1962, **12**, 652.

[5] For some detailed pharmacological data, see Buu-Hoï, Delbarre, Jacquignon, Rose, Sabathier, and Sinh, *Medicina Experimentalis*, 1962, **7**, 166.

the alcohols were more resistant to dehydration than the isomeric 1-(pyridyl)alkan-2-ols. Whereas the latter can be converted by heat into the corresponding pyridylalkenes, most of the 1-(pyridyl)alkan-1-ols distilled without decomposition under reduced pressure; attempts to dehydrate them with formic acid gave in many instances formic esters which were surprisingly stable and distilled without decomposition, except for the higher members which decomposed to give alkenylpyridines.

Experimental.—Preparation of the pyridylalkanols. To an ice-cooled Grignard reagent prepared from the appropriate alkyl halide (1·5 moles) and magnesium shavings (1·8 g.-atoms) in anhydrous ether (400 c.c.), a solution of the pyridine aldehyde (1 mole) in anhydrous ether

TABLE 1.

1-(Pyridyl)alkan-1-ols.

Substance	B. p./mm.	n_D (temp.) or m. p.	Formula	Found (%) C	Found (%) H	Found (%) N	Reqd. (%) C	Reqd. (%) H	Reqd. (%) N
			1-2′-*Pyridylalkan*-1-*ols*						
Propanol	113°/17	1·5206(29)	$C_8H_{11}NO$	69·7	8·2	10·5	70·0	8·1	10·2
Butanol	125/12	1·5152(21)	$C_9H_{13}NO$	71·2	8·7	9·6	71·5	8·7	9·3
Pentanol	132—135/15	1·5120(23)	$C_{10}H_{15}NO$	72·5	9·1	8·7	72·7	9·2	8·5
Hexanol	137—138/12	1·5045(23)	$C_{11}H_{17}NO$	73·4	9·9	8·0	73·7	9·6	7·8
Heptanol	155—156/16	1·5004(23)	$C_{12}H_{19}NO$	74·5	10·1	7·6	74·6	9·9	7·3
Octanol	163—164/13	1·4969(23)	$C_{13}H_{21}NO$	75·1	10·2	6·7	75·3	10·2	6·8
Nonanol	178—179/15	1·4922(24)	$C_{14}H_{23}NO$	75·8	10·8	6·2	76·0	10·5	6·3
Decanol	189—192/16	1·4840(24)	$C_{15}H_{25}NO$	76·4	10·8	5·9	76·5	10·7	6·0
Undecanol	196—198/15	M. p. 33°	$C_{16}H_{27}NO$	77·0	11·1	5·3	77·1	10·9	5·6
Dodecanol	207—209/15	M. p. 34°	$C_{17}H_{29}NO$	77·3	11·3	5·3	77·5	11·1	5·3
Tridecanol	215—217/15	M. p. 48°	$C_{18}H_{31}NO$	77·8	11·5	5·1	77·9	11·3	5·1
			1-3′-*Pyridylalkan*-1-*ols*						
Propanol	141—143/13	1·5242(23)	$C_8H_{11}NO$	69·8	8·4	10·5	70·0	8·1	10·2
Butanol	155—156/14	1·5178(22)	$C_9H_{13}NO$	71·6	8·6	9·6	71·5	8·7	9·3
Pentanol	168—170/17	1·5148(22)	$C_{10}H_{15}NO$	72·5	9·3	8·8	72·7	9·2	8·5
Hexanol	175—177/15	1·5128(21)	$C_{11}H_{17}NO$	73·5	9·6	8·1	73·7	9·6	7·8
Heptanol	184—185/15	1·5046(22)	$C_{12}H_{19}NO$	74·3	10·1	7·6	74·6	9·9	7·3
Octanol	192—194/15	1·5030(22)	$C_{13}H_{21}NO$	75·0	10·2	6·8	75·3	10·2	6·8
Nonanol	197—198/12	1·5018(19)	$C_{14}H_{23}NO$	75·8	10·8	6·4	76·0	10·5	6·3
Decanol	207—208/12	1·4980(19)	$C_{15}H_{25}NO$	76·4	10·8	6·1	76·5	10·7	6·0
Undecanol	—	M. p. 49°	$C_{16}H_{27}NO$	76·9	11·2	5·8	77·1	10·9	5·6
Dodecanol	—	M. p. 41°	$C_{17}H_{29}NO$	77·6	11·1	5·5	77·5	11·1	5·3
Tridecanol	—	M. p. 50°	$C_{18}H_{31}NO$	78·1	11·5	5·1	77·9	11·3	5·1
			1-4′-*Pyridylalkan*-1-*ols*						
Propanol	150—152/13	1·5233(19)	$C_8H_{11}NO$	70·1	8·3	10·1	70·0	8·1	10·2
Butanol	160/13	1·5199(22)	$C_9H_{13}NO$	71·3	8·9	9·6	71·5	8·7	9·3
Pentanol	177—178/18	1·5130(23)	$C_{10}H_{15}NO$	72·4	9·5	8·6	72·7	9·2	8·5
Hexanol	181—182/13	1·5118(23)	$C_{11}H_{17}NO$	73·5	9·7	8·0	73·7	9·6	7·8
Heptanol	186—187/16	1·5060(23)	$C_{12}H_{19}NO$	74·4	10·0	7·6	74·6	9·9	7·3
Octanol	186—188/13	1·4962(23)	$C_{13}H_{21}NO$	75·0	10·3	6·9	75·3	10·2	6·8
Decanol	—	M. p. 50°	$C_{15}H_{25}NO$	76·6	11·0	6·0	76·5	10·7	6·0
Undecanol	—	M. p. 60°	$C_{16}H_{27}NO$	76·8	11·0	5·7	77·1	10·9	5·6
Dodecanol	—	M. p. 52°	$C_{17}H_{29}NO$	77·6	11·3	5·2	77·5	11·1	5·3

(250 c.c.) was added in small portions with stirring, and the reaction was then completed by 10 minutes' refluxing. After cooling, the product was treated with cold aqueous ammonium chloride, the ethereal layer dried (Na_2SO_4), the solvent removed, and the residue fractionated *in vacuo*. The yields (30—70%) were highest when stirring was most vigorous. The *alcohols* obtained are listed in Table 1; those which were solid were recrystallised from hexane.

Esterification with formic acid. The alcohol (10 g.) was heated with formic acid (15 g.) for 30 min. on a water-bath; after cooling, aqueous sodium hydrogen carbonate was added, the product taken up in benzene, washed with water and aqueous sodium hydrogen carbonate, and dried (Na_2SO_4), the solvent removed, and the residue fractionated *in vacuo*. The pure *formyl esters* thus obtained are listed in Table 2.

1-3′-*Pyridyldodec*-1-*ene*. This *product*, obtained by repeated distillation of the corresponding

crude formate over alumina, formed leaflets, m. p. 43° (from ethanol), b. p. 227—228°/15 mm. (Found: C, 88·3; H, 10·7; N, 5·9. $C_{17}H_{27}N$ requires C, 83·2; H, 11·1; N, 5·7%); the picrate formed yellow prisms, m. p. 74°, from ethanol.

TABLE 2.

1-(Pyridyl)alkyl formates.

Ester of	B. p./mm.	n_D (temp.)	Formula	Found (%) C	H	O	Reqd. (%) C	H	O
1-3′-Pyridylbutan-1-ol	152—153°/20	1·5038(21)	$C_{10}H_{13}NO_2$	67·3	7·6	17·3	67·0	7·3	17·9
1-4′-Pyridylhexan-1-ol	176—177/18	1·5020(21)	$C_{12}H_{17}NO_2$	69·8	7·9	15·0	69·5	8·3	15·4
1-4′-Pyridylheptan-1-ol	186—188/18	1·4982(22)	$C_{13}H_{19}NO_2$	70·5	8·9	15·0	70·6	8·7	14·5
1-2′-Pyridyloctan-1-ol	183—185/29	1·4940(25)	$C_{14}H_{21}NO_2$	71·8	9·1	—	71·5	9·0	—
1-3′-Pyridyloctan-1-ol	198—200/30 *	1·4905(26)	$C_{14}H_{21}NO_2$	71·3	9·2	13·0	71·5	9·0	13·6
1-3′-Pyridylnonan-1-ol	210—212/30 †	1·4880(21)	$C_{15}H_{23}NO_2$	72·2	9·5	13·3	72·3	9·3	12·8
1-4′-Pyridylnonan-1-ol	213—214/32	1·4880(24)	$C_{15}H_{23}NO_2$	72·2	9·3	13·1	72·3	9·3	12·8

* *Picrate*, yellow needles, m. p. 66° (from ethanol) (Found: C, 52·0; H, 5·5. $C_{20}H_{24}N_4O_9$ requires C, 51·7; H, 5·2%). † *Picrate*, m. p. 73° (from ethanol) (Found: C, 52·6; H, 5·8; N, 11·6. $C_{21}H_{26}N_4O_9$ requires C, 52·7; H, 5·5; N, 11·7%).

INSTITUT DE CHIMIE DES SUBSTANCES NATURELLES DU C.N.R.S., GIF-SUR-YVETTE (S.-ET-O.).
CENTRE DE RECHERCHES SUR LES MALADIES OSTÉOARTICULAIRES (I.N.H.),
HÔPITAL COCHIN, PARIS, FRANCE. [*Received, February 19th*, 1963.]

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811. *The Co-ordination of Ethylenediaminetetra-acetate in Complexes of Cobalt*(III) *and Rhodium*(III).

By R. D. GILLARD and G. WILKINSON.

COMPLEXES containing ethylenediaminetetra-acetic acid (EDTA represents the fully ionized anion) or its analogues have been well studied by means of infrared spectroscopy in the solid state,[1] particular attention having been paid to the antisymmetric carboxylate stretching frequency. The conclusion has been that [1a] a band at ~1650 cm.$^{-1}$ is diagnostic of co-ordinated carboxylate groups, and a band at ~1750 cm.$^{-1}$ of free carboxyl groups. However, since the effect of lattice vibrations on these results is uncertain, we have measured the spectra of solutions of several complexes in heavy water. These are presented in the Table, together with solid-state frequencies for the same compounds for comparison.

In the cases examined here, the conclusions from spectra in the solid state, as to the occupation of co-ordination positions, are borne out by the spectra of solutions. In the case of aquo(ethylenediaminetriacetatoacetic acid)rhodium(III), the areas of the bands due to co-ordinated carboxylate and free carboxyl groups are roughly in the ratio 3 : 1, lending further support to the postulated quinquedentate nature of the ligand. Unfortunately, the bands due to co-ordinated carboxylate could not be located accurately in the quadridentate compounds of rhodium(III), although the bands due to free carboxyl were certainly stronger here than in the compound containing only one free carboxyl group.

Both the structure [2] and the infrared spectrum [1b] of the ethylenediaminetetra-acetatecobaltate(III) anion are known. The close correspondence (see Experimental section) of the infrared spectrum in solution with that of the ion in the solid state suggests that little change in the shape of the ion occurs on solution; presumably the diamine (*NN'*)-chelate ring is still in the *gauche* conformation in solution, as is also indicated by the nuclear magnetic resonance spectrum. The *gauche* nature of the *NN'*-chelate ring in the analogous

[1] (*a*) For references see Cotton in "Modern Coordination Chemistry," ed. Lewis and Wilkins, Interscience Publ. Inc., New York, 1960, p. 390; (*b*) Busch and Bailar, *J. Amer. Chem. Soc.*, 1953, **75**, 4574; (*c*) Gillard, *Nature*, 1960, **188**, 487; (*d*) Dwyer and Garvan, *J. Amer. Chem. Soc.*, 1960, **82**, 4823.
[2] Weakliem and Hoard, *J. Amer. Chem. Soc.*, 1959, **81**, 550.

propylenediaminetetra-acetatocobaltate(III) anion (PDTA in Table) in solution has been demonstrated by mechanistic studies.[3]

Experimental.—Microanalyses were by the Microanalytical Department of this College.

Compounds were prepared by the methods referred to in the Table; their purity was confirmed by infrared and electronic spectroscopy. The following were analysed: aquo(ethylenediaminetriacetatoacetic acid)rhodate(III) (Found: C, 29·2; H, 3·9; N, 6·8. Calc. for

The antisymmetric carboxyl region for EDTA complexes.

Anion *	Prep.	Conditions	CO_2M	CO_2H	Co-ordn. posn. †	Ref.
$[Co(EDTA)]^-$	*A*	Mull	1638	—	6	1*b*
		D_2O	1630	—	6	
$[Co(HEDTA)Br]^-$		Mull	1628	1723	5	1*b*
$[Co(\pm PDTA)]^-$	*B*	Mull	1647	—	6	1*c*
		D_2O	1638	—	6	
$(-)$-$[Co(+PDTA)]^-$	*B*	Mull	1647	—	6	1*c*
		D_2O	1637	—	6	
$[Rh(HEDTA)(H_2O)]$		Mull ‡	1643	1742	5	1*d*
		D_2O	1641	1727	5	
$[Rh(H_2EDTA)Cl_2]^-$		Mull ‡	1598	1720	4	1*d*
		D_2O	—	1718	4	
$[Rh(H_2EDTA)Br_2]^-$		Mull ‡	1595	1717	4	1*d*
		D_2O	—	1713	4	

* Compounds were recrystallized once from D_2O before solution spectra were taken. † Occupation of co-ordination positions by the ligand. ‡ These solid-state spectra have been checked in this work.

(*A*) See Dwyer, Gyarfas, and Mellor, *J. Phys. Chem.*, 1955, **59**, 296. (*B*) See Dwyer and Garvan, *J. Amer. Chem. Soc.*, 1959, **81**, 2955.

$C_{10}H_{15}N_2O_9Rh$: C, 29·3; H, 3·7; N, 6·8%); potassium dichloro(ethylenediaminediacetatodiacetic acid)rhodate(III) (Found: Cl, 14·0. Calc. for $C_{10}H_{14}Cl_2KN_2O_8Rh$: Cl, 14·1%); potassium dibromo(ethylenediaminediacetatodiacetic acid)rhodate(III) (Found: Br, 26·8. Calc. for $C_{10}H_{14}Br_2KN_2O_8Rh$: Br, 27·0%).

Infrared spectra were obtained using a Perkin-Elmer model 21 spectrometer, with mulls or thin films between silver chloride plates, in either water (from 1300—1100 $cm.^{-1}$) or heavy water (2000—1300 and 1100—750 $cm.^{-1}$).

Anhydrous potassium ethylenediaminetetra-acetatocobaltate(III) showed infrared bands below 1500 $cm.^{-1}$ in aqueous solution at 1461w, 1439w, 1350s, 1087w, 1065m, 1015w, 994w, 934w, 913m, 882m, and 836w $cm.^{-1}$; the corresponding bands in mulls appeared at 1468m, 1445m, 1351s, 1090w, 1067m, 1019w, 994w, 950m, 928s, 884m, and 847m $cm.^{-1}$. Peaks corresponding to those found in mulls at 1313, 1287, 1273, and 1255 $cm.^{-1}$ were not observed in solution.

The infrared spectra, of mulls, in the sodium chloride region of the compounds of rhodium(III) studied are given below, in $cm.^{-1}$

$[Rh(HEDTA)(H_2O)]$. In addition to the γ-OH stretch at 3420s, weak bands occurred at 2723, 2611, and 2537, presumably due to hydrogen bonding in the crystal. Other bands occurred at: 1322w, 1314m, 1271m, 1225s, 1160m, 1087s, 1063m, 1044m, 1008w, 1000m, 981w, 964w, 949vw, 934s, 915s, 901m, 882s, 821s, 766m, and 739w.

$K[Rh(H_2EDTA)Cl_2]$: 1320m, 1303m, 1271w, 1242w, 1218s, 1159w, 1081m, 1017m, 1011sh, 972w, 926w, 890m, 828s, and 787m.

$K[Rh(H_2EDTA)Br_2]$: 1317m, 1300m, 1270w, 1236w, 1216s, 1156w, 1079m, 1016m, 1010sh, 970w, 924w, 889w, 827s, and 782m.

We thank Dr. W. P. Griffith for help in running some spectra, and Johnson, Matthey and Co. Ltd. for a gift of rhodium metal.

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LONDON, S.W.7.

[*Received, February 19th*, 1963.]

[3] Busch, Cooke, Swaminathan, and Im, " Advances in the Chemistry of the Coordination Compounds," ed. Kirschner, Macmillan, London, 1961, p. 139.

812. *The Transition State in the Acid-catalysed Hydrolysis of Benzamide.*

By R. B. Moodie, (Miss) P. D. Wale, and (Miss) T. J. Whaite.

Bunnett [1] has recently re-established the Hammett acidity function as a valuable criterion of mechanism by the use of w values as in equation (1) (applicable to weakly basic substrates). For acid-catalysed amide hydrolysis, a correction must be made for the partial protonation of the substrate at the acid concentrations used. Equation (2), as used by Bunnett, requires that the protonation equilibria can be expressed by equation (3).

$$\log k_{obs} + H_0 = w \log a_{H_2O} + \text{Constant.} \quad (1)$$

$$\log k_{obs} + \log [h_0/(K_{SH^+} + h_0)] = w \log a_{H_2O} + \text{Constant.} \quad (2)$$

$$pH_{SH^+} = H_0 + \log ([SH^+]/[S]). \quad (3)$$

However, amide-protonation equilibria give results deviating considerably from equation (3).[2-4] This, and the fact that the value for pK_{SH^+} of benzamide used by Bunnett is $-0{\cdot}77$, which is quite different from the reported [5] value of $-2{\cdot}16$, throws doubt on the numerical value and possibly the significance of w for this compound.

We have studied the protonation of benzamide in aqueous perchloric acid. The isosbestic point is better defined than in aqueous sulphuric acid, which permits a more

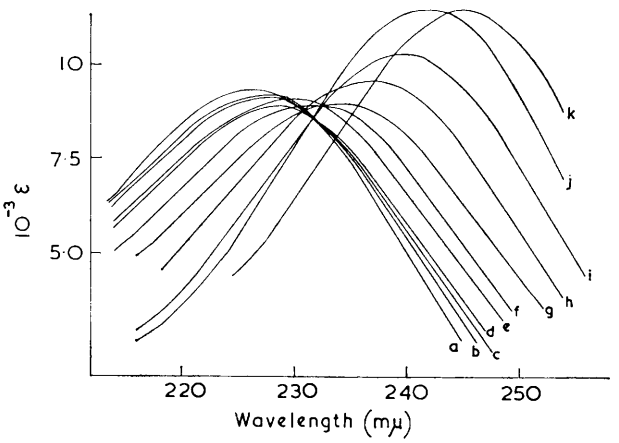


Fig. 1. Spectrum of benzamide in aqueous perchloric acid solutions of the following molarities: (a) 0, (b) 1·07, (c) 1·63, (d) 2·24, (e) 2·90, (f) 3·60, (g) 4·41, (h) 5·15, (i) 6·12, (j) 7·06, (k) 9·16.

accurate spectrophotometric determination of the ionisation ratio. A wavelength shift, but no change in extinction coefficient, was noted in the spectrum of the protonated compound at high acidities (Fig. 1). Two plots of the Davis and Geissman type,[5,6] for different wavelengths, gave H_0 values for half-protonation of $-2{\cdot}10$ and $-2{\cdot}20$. These agree well with the reported value [5] of $-2{\cdot}16$. An error in the pK of the magnitude implied by Bunnett therefore seems unlikely. A plot of log ($[SH^+]/[S]$) against H_0 gave a straight line with a slope of 0·74. This low value, common to all amides so far studied,[2-4] indicates extensive hydration of the protonated amide (this point is discussed elsewhere [4]). A similar value for the slope was found for benzamide in aqueous sulphuric

[1] Bunnett, *J. Amer. Chem. Soc.*, 1961, **83**, 4956, 4968, 4973, 4978.
[2] Edward and Wang, *Canad. J. Chem.*, 1962, **40**, 966.
[3] Stewart, personal communication.
[4] Homer and Moodie, *J.*, in the press.
[5] Edward, Chang, Yates, and Stewart, *Canad. J. Chem.*, 1960, **38**, 1518.
[6] Davis and Geissman, *J. Amer. Chem. Soc.*, 1954, **76**, 3507.

acid.[3] We have assumed that the ionisation ratio in the two aqueous acids of the same H_0 is the same and have used equation (4), derived below, to correlate the published data [7] for the kinetics of the hydrolysis of benzamide in aqueous sulphuric acid at 25°.

For the reaction

$$SH^+(H_2O)_a + bH_2O \xrightarrow{k} {}^{\ddagger}(H_2O)_{(a+b)},$$

$$\text{Rate} = k_{obs}([SH^+] + [S]) = k[SH^+] \cdot a_{H_2O}{}^b \cdot f_{SH^+}/f^{\ddagger}.$$

k_{obs} is the observed first-order rate constant, and activity coefficients refer to hydrated species. It follows that

$$\log k_{obs} + \log (1 + [S]/[SH^+]) = \log k \cdot f_{SH^+}/f^{\ddagger} + b \log a_{H_2O}. \quad (4)$$

Equation (4) involves neither the Hammett acidity function nor an arbitrary value of pK_{SH^+}. Fig. 2 shows a plot of $[\log k_{obs} + \log (1 + [S]/[SH^+])]$ against $-\log a_{H_2O}$. If the activity-coefficient term in equation (4) is assumed constant, the slope of this line gives the value of b, the number of water molecules in addition to the hydration sheath of the protonated amide, needed to form the activated complex.

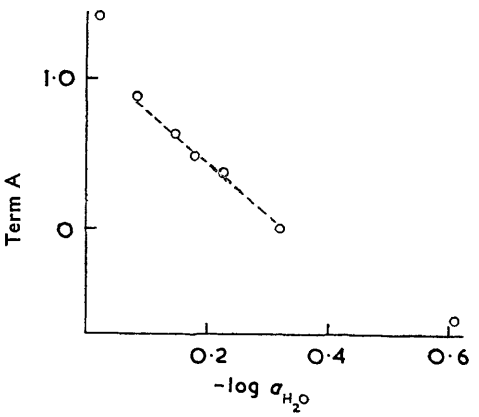
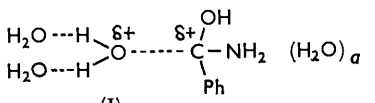


FIG. 2. Plot of $[\log k_{obs} + \log (1 + [S]/[SH^+])]$ (A) against $-\log a_{H_2O}$.

Fig. 2 shows that this value, b, decreases with decreasing water activity, *i.e.*, with increasing acid concentration. The straight central portion gives $b = 3{\cdot}3$. This suggests that in this limited region of acidity (30—45% sulphuric acid) the transition state is (I).



(I)

The decrease of b with increasing acidity is in accord with the decrease in hydration numbers of protonated amides with increasing acidity.[2,4]

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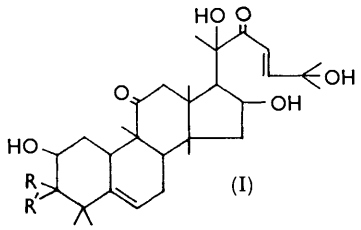
[*Received, February* 21*st*, 1963.]

[7] Edward and Meacock, *J.*, 1957, 2000.

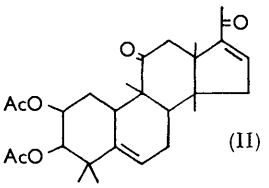
813. *Bitter Principles of the Cucurbitaceae. Part XII.*[1] *The Constitution of Cucurbitacin F.*

By K. J. VAN DER MERWE, P. R. ENSLIN, and K. PACHLER.

CUCURBITACIN F, $C_{30}H_{46}O_7$ (previously[2] reported as $C_{30}H_{48}O_7$), occurs in the leaves of *Cucumis dinteri* Cogn. in association with cucurbitacin D, for which the structure (I; R,R′ = O) has recently[1] been proposed. Cucurbitacin F contains an αβ-unsaturated ketone group [$\lambda_{max.}$ 232 mμ, ε 11,200; $\nu_{max.}$ (in KBr) 1690 and 1629 cm.$^{-1}$] and an isolated ketone group [$\lambda_{max.}$ 300 mμ, ε 128; $\nu_{max.}$ (in KBr) 1700 cm.$^{-1}$]. Hydrogenation over palladised calcium carbonate in ethanol gave a dihydro-derivative in which the conjugated double bond had been saturated. Cucurbitacin F consumed two mol. of periodic acid, as did cucurbitacin D; however, no colour reaction was given with Tetrazolium Blue, indicating the absence of an α-ketol system in ring A of cucurbitacin F. This evidence and the presence in cucurbitacin F of two hydrogen atoms more than in cucurbitacin D suggested the structure (I; R = H, R′ = OH) for cucurbitacin F, which is confirmed by the following experiments.



(I)



(II)

Acetylation of cucurbitacin F gave an amorphous product which consumed one mol. of periodic acid to give *trans*-4-acetoxy-4-methylpent-2-enoic acid[3] and a material which, on treatment with alkali and reacetylation, gave an anhydrohexanor-compound, $C_{28}H_{38}O_6$, formulated as (II) on the following evidence. The compound contained an αβ-unsaturated ketone group ($\lambda_{max.}$ 240 mμ, ε 11,300). The nuclear magnetic resonance spectrum showed two acetate methyl groups (τ 7·97 and 8·04), a methyl ketone (τ 7·73), and five quaternary methyl groups (τ 8·87, 8·94, 8·96, 9·01, and 9·08). The 12-methylene protons were found as a single peak at τ 6·99. The two secondary ester protons occurred as a complex ABXY-pattern centred around τ 5·19. Of the two olefinic protons, that at position 6 showed a multiplet (τ 4·28) due to coupling with protons at positions 7 and 10, and that at position 16 showed a triplet (τ 3·36, J = 2·7 c./sec.). The steric conformation of the ring-A hydroxyl groups was determined by analysis of the ABXY-pattern, which gave the following results: $\Delta\nu_{AB}$ = 20·9; J(AB) = 10·3; J(AX) = 10·3; J(AY) = 4·3 c./sec.; J(BX) = J(BY) = 0. The two protons A and B are, therefore, both in the axial position, showing a large coupling constant of 10·3 c./sec.[4] Further, the A proton at lower field showed axial–axial (J = 10·3 c./sec.) and axial–equatorial (J = 4·3 c./sec.) splitting by the neighbouring methylene group.

A direct correlation of cucurbitacin F with cucurbitacin D was accomplished by reduction of dihydrocucurbitacin D[5] with sodium borohydride to dihydrocucurbitacin F.

Experimental.—Unless specified to the contrary, $[\alpha]_D$ and ultraviolet absorption spectra refer to ethanol, and infrared spectra to chloroform solutions. Infrared spectra were determined on a Perkin-Elmer model 21 spectrometer and ultraviolet absorption spectra on a Unicam

[1] de Kock, Enslin, Norton, Barton, Sklarz, and Bothner-By, *J.*, 1963, 3828, is regarded as Part XI of this series.
[2] Enslin, Rehm, and Rivett, *J. Sci. Food Agric.*, 1957, **8**, 673.
[3] Enslin, Hugo, Norton, and Rivett, *J.*, 1960, 4779.
[4] Lemieux, Kullnig, Bernstein, and Schneider, *J. Amer. Chem. Soc.*, 1957, **79**, 1005.

S.P. 500 spectrometer. The nuclear magnetic resonance spectrum was determined in deuteriochloroform solution (~3 mol. %) on a Varian A-60 spectrometer. The chemical shifts were measured on the τ-scale relative to tetramethylsilane as internal standard (τ 10·0); τ-values are estimated to be accurate to ±0·01 p.p.m., coupling constants to ±0·2 c./sec.

Cucurbitacin F. The crude bitter principle was isolated from the leaves of *Cucumis dinteri* Cogn. as described before.[2] The pure *compound* crystallised from dry chloroform as needles, m. p. 244—245°, $[\alpha]_D$ +38° (*c* 1·2) (Found: C, 69·2; H, 9·3. $C_{30}H_{46}O_7$ requires C, 69·5; H, 8·9%).

Cucurbitacin F (150 mg.) in ethanol (10 ml.) and 0·1M-periodic acid (7 ml.) consumed 1·9 mol. of reagent when kept at room temperature in the dark for 50 hr.

Dihydrocucurbitacin F. Cucurbitacin F (52 mg.) was hydrogenated over 5% palladised calcium carbonate (25 mg.) in ethanol (10 ml.) (0·98 mol. absorbed in 15 min.). Crystallisation of the product from chloroform gave *dihydrocucurbitacin F* (34 mg.), m. p. 155—156°, $[\alpha]_D$ +48° (*c* 1·3), $\nu_{max.}$ (KBr) 1694 cm.$^{-1}$ (Found: C, 68·9; H, 9·0. $C_{30}H_{48}O_7$ requires C, 69·2; H, 9·3%).

Dihydrocucurbitacin F from cucurbitacin D. Cucurbitacin D (350 mg.) was hydrogenated over 5% palladised calcium carbonate (70 mg.) in ethanol (40 ml.) (0·93 mol. absorbed in 25 min.) to give the crude dihydro-derivative. To a solution of dihydrocucurbitacin D (340 mg.) in methanol (10 ml.) was added a solution of sodium borohydride (75 mg.) in methanol (10 ml.), and the mixture kept at room temperature under nitrogen for 1 hr. The excess of sodium borohydride was decomposed with dilute hydrochloric acid, and the mixture diluted with water (20 ml.) and extracted with chloroform. The product (290 mg.) was purified by chromatography on silica (F. Smith; 100 g.). Elution with 4 : 1 chloroform–methanol and crystallisation from chloroform gave dihydrocucurbitacin F (170 mg.), m. p. and mixed m. p. 155—156°, $[\alpha]_D$ +49° (*c* 1·2), infrared spectra identical.

The physical constants of the above dihydrocucurbitacin F are very similar to those of a tetrahydrocucurbitacin D, m. p. 152—156°, $[\alpha]_D$ +31° (in EtOH), and hexahydrocurbitacin I, m. p. 156—157°, $[\alpha]_D$ +49° (in $CHCl_3$), first prepared by Lavie *et al.*[5,6] These compounds must be epimeric with dihydrocucurbitacin F at C-2 and/or C-3, since their infrared spectra and that of dihydrocucurbitacin F showed small but significant differences near 1000 cm.$^{-1}$. Tetrahydrocucurbitacin D was prepared according to Lavie *et al.*[5] and an authentic sample of hexahydrocucurbitacin I was kindly supplied by Professor D. Lavie.

Periodic acid oxidation of acetylated cucurbitacin F. Cucurbitacin F (3 g.) was boiled for 1·5 hr. in acetic anhydride under nitrogen. To a solution of the amorphous product in ethanol (200 ml.) was added 0·1M-periodic acid (150 ml.), and the mixture was kept in the dark for 120 hr. (0·8 mol. of periodic acid consumed). The excess of reagent was destroyed with ethylene glycol (15 ml.), and the mixture concentrated *in vacuo* to turbidity. After addition of water (80 ml.) and saturated sodium hydrogen carbonate solution (100 ml.), extraction with chloroform gave a neutral fraction (1·8 g.). The acidified aqueous layer was extracted with ether, to give an oil (200 mg.) which crystallised from ether and sublimed *in vacuo* at 70° to afford *trans*-4-acetoxy-4-methylpent-2-enoic acid, m. p. 84·5°, identified by mixed m. p. and infrared spectrum.

The above neutral fraction was dissolved in 0·1N-sodium hydroxide in 70% ethanol (60 ml.) and kept overnight at room temperature. After acidification with dilute hydrochloric acid and isolation with chloroform, an oil was obtained which was acetylated in boiling acetic anhydride. Filtration of the product through acid-washed alumina (100 g.) with 6 : 1 benzene–chloroform, crystallisation from ether, and sublimation *in vacuo* at 180° gave Δ^{16}-*anhydrohexanorcucurbitacin F diacetate*, m. p. 211—215°, $[\alpha]_D$ +61° (*c* 3·7 in $CHCl_3$), $\lambda_{max.}$ 240 mμ (ε 11,300), $\nu_{max.}$ 1740, 1696, 1666, and 1596 cm.$^{-1}$ (Found: C, 71·3; H, 8·4. $C_{28}H_{38}O_6$ requires C, 71·5; H, 8·1%).

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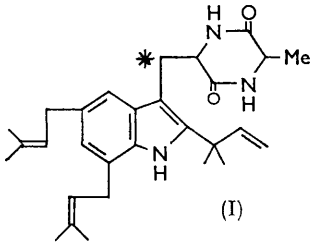
SOUTH AFRICAN COUNCIL FOR SCIENTIFIC AND INDUSTRIAL RESEARCH,
PRETORIA, SOUTH AFRICA. [*Received, February 28th,* 1963.]

[5] Lavie and Shvo, *J. Amer. Chem. Soc.*, 1959, **81**, 3058.
[6] Lavie and Willner, *J. Amer. Chem. Soc.*, 1958, **80**, 710.

814. *Studies in Relation to Biosynthesis. Part XXXIII.* Incorporation of Tryptophan into Echinulin.*

By A. J. Birch and (Mrs.) K. R. Farrar.

Previous work [1] with [^{14}C]-labelled precursors indicates that echinulin (I) arises in part from alanine and three isoprene units. The main nucleus is presumably that of tryptophan, and among the processes involved may therefore be the direct insertion of C_5-units into the aromatic system. There is considerable presumptive evidence [2] that such alkylations occur widely, but the only results involving direct incorporations of labelled precursors bearing on the problem are concerned with the ergot alkaloids. Here the nucleus is certainly derived from tryptophan and a terpene unit, but there is at present a conflict of results as to whether the latter is inserted initially into the nucleus [3,4] or into the side-



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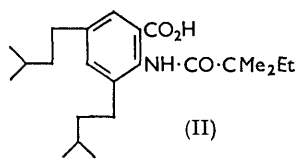

(II)

chain.[5] In the case of echinulin, if the nucleus is shown to be derived from tryptophan there is no further doubt that direct alkylation of the aromatic system must occur. Our results strongly support an origin from tryptophan.

DL-[1-^{14}C]Tryptophan was found to be incorporated into echinulin by *Aspergillus amstelodami* to the extent of 1·36% (or 2·72% if only L-tryptophan is involved). Echinulin from this source (r.m.a. $6{\cdot}57 \times 10^4$) was hydrolysed by hydrobromic acid,[6] and the alanine isolated was practically inactive (r.m.a. $1{\cdot}26 \times 10^2$), so that little incorporation had occurred into this part of the molecule by degradation of the tryptophan. If the side-chain of the tryptophan had been removed as serine, the alanine would have been expected to possess considerable labelling.

Echinulin [r.m.a. $9{\cdot}9 \times 10^3$; expected labelling as in (I); * = ^{14}C] was converted by hydrolysis of the dioxopiperazine ring into a potassium salt, which on pyrolysis [7] gave, with loss of the side-chain, the indole mixture described by Quilico *et al.* [7] (r.m.a. $3{\cdot}9 \times 10^3$). A considerable, but not complete, loss of activity has occurred in this process and it appears that probably the material still contains a proportion of an indole carrying the 1′-carbon, possibly as a methyl group. This was confirmed by hydrogenation of the side-chain double bonds of the mixture and oxidation [8] to the acid (II) which was then almost devoid of activity (r.m.a. $2{\cdot}1 \times 10^2$). The acid (II) was identified by its method of preparation and its m. p. (125—127°) and spectra ($\lambda_{max.}$ 296, 216 mμ; log ε 3·55, 4·31) [lit.,[7,8] m. p. 127°; $\lambda_{max.}$ 296, 216 mμ (log ε 3·55, 4·38)]. This result also indicates that the terpene chains contain negligible activity and supports the assumption that the radioactivity of the precursor has not been transferred to the echinulin by removal and transfer of the tryptophan side-chain, since considerable labelling of acetyl-coenzyme-A would then be expected.

* Part XXXII, *J.*, 1963, 2209.

[1] Birch, Blance, David, and Smith, *J.*, 1961, 3128.
[2] *E.g.*, Birch, *Fortschr. Chem. Org. Naturstoffe*, Springer, Vienna, 1957, Vol. XIV, p. 200.
[3] Plieninger, Fischer, and Liede, *Angew. Chem.*, 1962, **74**, 430.
[4] Baxter, Kandel, Okany, and Tam, *J. Amer. Chem. Soc.*, 1962, **84**, 4350.
[5] Weygand, Floss, and Mothes, *Tetrahedron Letters*, 1962, 873.
[6] Quilico, Cardani, and Piozzi, *Gazzetta*, 1956, **86**, 211.
[7] Quilico, Cardani, and Piozzi, *Gazzetta*, 1955, **85**, 3.
[8] Casnati, Cavalleri, Piozzi, and Quilico, *Gazzetta*, 1962, **92**, 105.

An interesting structural feature of echinulin is the reversed terpene unit in the 2-position. Mechanistically this type of incorporation is quite acceptable, but the orientation is unusual and may possibly arise by preliminary normal alkylation on the indole nitrogen and cyclic rearrangement.

Experimental conditions and equipment were as previously described.[1]

We are indebted to Professor Quilico for a gift of echinulin and to the Rockefeller Foundation for financial assistance.

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MANCHESTER. [*Received, February 28th*, 1963.]

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815. *The Participation of Chemisorbed Molecules in Catalysis.*

By S. J. THOMSON and J. L. WISHLADE.

WHEN molecules are chemisorbed on the surface of a catalyst, the problem arises whether the molecules that will subsequently be involved in catalytic reaction are those adsorbed in the early or in the later stages of the chemisorption process. We have made a preliminary investigation of this problem by our technique [1] of direct observation of the

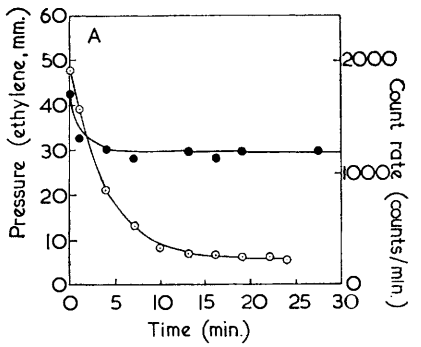

FIG. 1A.

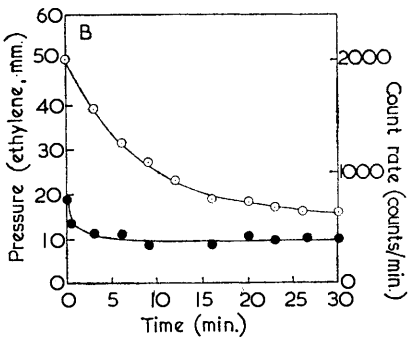

FIG. 1B.

FIG. 1. The surface count rate during the hydrogenation of ethylene at 20°, for a nickel film partially covered with ethylene, then with [^{14}C]ethylene: (A) film 21, (B) film 22.

○ Pressure. ● Count rate.

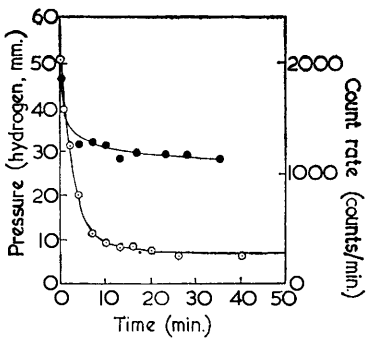

FIG. 2. The surface count rate during hydrogenation of ethylene at 20°, for nickel film partially covered with [^{14}C]ethylene, then with normal ethylene.

○ Pressure. ● Count rate.

behaviour of radioactively labelled molecules on the surface of a catalyst. In this method, a Geiger–Müller counter [2] is arranged to monitor directly the β-emission from ^{14}C-labelled

[1] Thomson and Wishlade, *Trans. Faraday Soc.*, 1962, **58**, 1170.
[2] Thomson and Wishlade, *J. Sci. Instr.*, 1962, **39**, 570.

molecules on the surface. Thus, in the experiments to be described, inactive ethylene was adsorbed on an evaporated nickel film to partial coverage, and this was followed by saturation of the film with [^{14}C]ethylene. The behaviour of the [^{14}C]ethylene could then be observed during subsequent hydrogenation of inactive ethylene. The surface count rate during this kind of experiment is shown in Fig. 1. Here the [^{14}C]ethylene, which was admitted second, is involved in the subsequent hydrogenation, for the surface count rate fell by 34% and 46% in two experiments.

When the order of admission of the gases to the catalyst surface was reversed, *i.e.*, [^{14}C]ethylene followed by inactive ethylene, the surface count behaviour was as shown in Fig. 2. Here the surface count rate fell by 45%. This indicated that the [^{14}C]ethylene admitted in the early stages of a chemisorption was also involved in subsequent catalysis.

Thus it appears that the ethylene molecules admitted in both the early and the late stage of chemisorption were involved in subsequent catalytic changes, either themselves, or as the fragments they formed.[3,4] We exclude molecular exchange as a possible explanation of the fall in surface count rates. We favour an explanation which arises from a consideration of field emission microscopy experiments for ethylene on iridium, wherein Arthur and Hansen [5] have shown that ethylene is immobile. Thus it is possible that, in the case of nickel, the ethylene molecules arrive at a variety of nickel crystal faces where they have a high sticking probability and are immobile once they have been adsorbed: if catalytic changes take place on only some of these crystal faces, then only a fraction of the chemisorbed ethylene molecules would be removed, no matter at what stage they were initially chemisorbed.

Experimental.—The adsorptions and hydrogenations were performed at 20° in an apparatus previously described.[1] The results obtained were as follows for film 21 (results for film 22 are in parentheses). 1·45 (2·17) cm.^{3} mm. mg.$^{-1}$ of inactive ethylene were admitted first to this film, weight 29·0 (38·3) mg. After 30 minutes' evacuation at 10^{-4} mm., 3·45 (0·81) cm^3 mm. mg.$^{-1}$ of [^{14}C]ethylene of specific activity 0·0905 mc/mmole were admitted. After evacuation of the gas-phase ethylene, Geiger–Müller counts showed that 1·83 (0·62) cm.^{3} mm. mg.$^{-1}$ of [^{14}C]-ethylene had been adsorbed. Hydrogen and ordinary ethylene, to pressures of 52·1 (132) and 47·6 (50) mm. were admitted to the film: hydrogenation started at $1{\cdot}99 \times 10^{20}$ ($7{\cdot}11 \times 10^{19}$) molecules min.$^{-1}$ mg.$^{-1}$. The surface count rate from [^{14}C]ethylene fell during this hydrogenation by 34% (46%). The results are shown in Fig. 1.

The first gas to be admitted to film 19, 38·8 mg., was 1·56 cm.^{3} mm. mg.$^{-1}$ of [^{14}C]ethylene. The count rate showed that 1·14 cm.^{3} mm. mg.$^{-1}$ of [^{14}C]ethylene had been adsorbed. We deduced that further ethylene was adsorbed, when the film was saturated with ordinary ethylene, as follows. Since films 21 and 22, which had been exposed to 1·45 and 2·17 cm.^{3} mm. of ethylene per mg. of film, subsequently adsorbed, respectively, 1·83 and 0·62 cm.^{3} mm. of [^{14}C]-ethylene, film 19 probably adsorbed 1—1·5 cm.^{3} mm. mg.$^{-1}$ of ordinary ethylene in the second stage. Subsequent hydrogenation, when ethylene and hydrogen were admitted, to pressures of 51·3 and 50·3 mm., respectively, was initially at the rate of $1{\cdot}44 \times 10^{20}$ molecules min.$^{-1}$ mg.$^{-1}$. The counter monitoring the surface during the hydrogenation of ethylene again showed a fall in count rate of 45% (Fig. 2).

We acknowledge gratefully a D.S.I.R. maintenance grant (to J. L. W.) and their grant towards purchase of equipment.

CHEMISTRY DEPARTMENT,
THE UNIVERSITY, GLASGOW, W.2. [*Received, January* 1*st*, 1963.]

[3] Little, Sheppard, and Yates, *Proc. Roy. Soc.*, 1960, *A*, **259**, 242.
[4] McKee, *J. Amer. Chem. Soc.*, 1962, **84**, 1109.
[5] Arthur and Hansen, *J. Chem. Phys.*, 1962, **36**, 2062.

816. *Synthesis of Aliphatic Isocyanides.*

By J. CASANOVA, jun., R. E. SCHUSTER, and N. D. WERNER.

A STUDY of the kinetics and stereochemistry of the isocyanide–nitrile rearrangement in our laboratories [1] demanded a method for the reliable preparation of very pure aliphatic isocyanides. Although many methods were available for the synthesis of both aliphatic [2a–f] and aromatic [2a,c,g] isocyanides, none was suitable for our requirements. In the dehydration of *N*-alkylformamides by an acid halide and a base,[2a] considerable loss of isocyanides of low molecular weight occurs during the extraction from water into pentane, probably because of the strong hydrogen bonding between isocyanides and hydroxylic compounds.[3] Efficient separation of the isocyanide from pentane and from pyridine is also difficult.

Efforts to prepare pure aliphatic isocyanides, by the addition of dichlorocarbene to primary amines,[2g,4] were frustrated because separation of unchanged amine from the corresponding isocyanide proved impractical, again owing to similarity in boiling points and strong hydrogen-bonding between these species.[3] Removal of the excess of amine by acid washing was precluded by the reaction—often violent—between isocyanides and strong acids.[5] Thus, although the reaction of hexachloroacetone and a strong base [6] (*e.g.*, sodium methoxide, sodium amide, lithium diethylamine, or potassium t-butoxide) with several amines was satisfactory for the generation of isocyanides, none of these procedures was suitable for the isolation of pure samples.

By a modification of existing methods which are based upon dehydration of an *N*-substituted formamide by an acid halide in the presence of a base,[2a,b] fair to good yields of several aliphatic isocyanides have been obtained. Purity of the crude products exceeds 98%, and the procedure is expeditious. The reaction may be conducted entirely in standard vacuum-line apparatus, an advantage for isocyanide preparations. The technique also has been applied to the preparation of heat-sensitive isocyanides.

When an *N*-alkylformamide is added slowly to a warm mixture of toluene-*p*-sulphonyl chloride and quinoline, dehydration occurs smoothly, as shown by rapid distillation of isocyanide into a cold receiver:

$$R{\cdot}NH{\cdot}CHO + p\text{-}C_6H_4Me{\cdot}SO_2Cl + 2C_9H_7N \longrightarrow RNC + 2C_9H_7N^+ + p\text{-}C_6H_4Me{\cdot}SO_3^- + Cl^-$$

The product is removed as it is formed by the application of a moderate vacuum to the system. The large difference in boiling point between reactants and product facilitates its complete separation in this operation. This technique serves both to indicate the progress of the reaction and to avoid detrimental effects of excessive heat on the isocyanide.[7] Products are then degassed and transferred by standard high-vacuum procedures. It is upon once-transferred samples that the analyses of chemical purity are based.

Experimental.—Ethyl formate was Eastman's Practical Grade and was fractionally distilled. Quinoline was Matheson, Coleman, and Bell's Refined Grade and was vacuum-distilled from zinc dust. Toluene-*p*-sulphonyl chloride, *N*-ethylformamide, and s-butylamine were Eastman's White Label, and were used without purification. *N*-Methylformamide was Pure Grade from Fluka, A.G., and was used without purification.

Methyl isocyanide. *N*-Methylformamide (15·0 g., 0·25 mole) was added dropwise in a 10 min. period to a stirred solution of toluene-*p*-sulphonyl chloride (72·5 g., 0·38 mole) and quinoline

[1] Presented before the Organic Division, Amer. Chem. Soc. 144th Nat. Meeting, Los Angeles, California, Spring, 1963.

[2] (*a*) Ugi and Meyr, *Chem. Ber.*, 1960, **93**, 239; *Org. Synth.*, 1961, **41**, 13, 101. (*b*) Hertler and Corey, *J. Org. Chem.*, 1958, **23**, 1221; Hofmann, *Annalen*, (*c*), 1867, **144**, 238; (*d*) 1868, **146**, 107; (*e*) Gautier, *Ann. Chim. Phys.*, 1869, **17**, 108; (*f*) Jackson and McCusick, *Org. Synth.*, 1955, **35**, 62; (*g*) Krapcho, *J. Org. Chem.*, 1962, **27**, 1089.

[3] Schleyer and Allerhand, *J. Amer. Chem. Soc.*, 1962, **84**, 1322; Ferstandig, *ibid.*, pp. 1323, 3553.

[4] Hine, *J. Amer. Chem. Soc.*, 1950, **72**, 2438.

[5] Sedgwick, "The Chemical Elements and Their Compounds," Oxford Univ. Press, 1950, Vol. I, p. 673.

[6] Grant and Cassie, *J. Org. Chem.*, 1960, **25**, 1433.

[7] Guillemard, *Compt. rend.*, 1907, **144**, 141.

(129 g., 1·00 mole) at 75°/60 mm. Methyl isocyanide (5·2 g., 0·13 mole) distilled rapidly and was collected in a receiver cooled by liquid nitrogen. Gas–liquid chromatography of this material indicated a purity of 99% (polypropylene glycol–firebrick; 2 m.; 75°; retention volume, 55 c.c. of helium). The product had an infrared maximum at 2170 cm.$^{-1}$ (100 mm. path; gas sample; 20 mm. pressure) (lit.,[8] 2166 cm.$^{-1}$).

Ethyl isocyanide. In a similar reaction, *N*-ethylformamide (18·3 g., 0·25 mole) gave 99% pure isocyanide, $\nu_{max.}$ 2151 cm.$^{-1}$ (lit.,[9] 2183—2144 cm.$^{-1}$).

s-Butyl isocyanide. s-Butylformamide (6·8 g., 0·067 mole), b. p. 60—61°/0·5 mm. (lit.[10] b. p. 110—114°/18 mm.), was prepared in 96% yield by aminolysis of ethyl formate with s-butylamine, in the presence of a trace of toluene-*p*-sulphonic acid.* The formamide was converted as above into 98% pure *s-butyl isocyanide* (35%), $\nu_{max.}$ 2125 cm.$^{-1}$ (in CCl_4) [9] (Found: C, 72·8; H, 10·7; N, 17·0. C_5H_9N requires C, 72·2; H, 10·9; N, 16·85%).

Cyclobutylformamide. Cyclobutylamine, b. p. 79—81° (lit.,[12] 82—83°) was prepared by a Schmidt reaction of cyclobutanecarboxylic acid.[12] The amine was converted as described earlier [11] into *cyclobutylformamide* (93%), b. p. 72·8—75·0°/0·8 mm., $\nu_{max.}$ 3330s, 1670s, and 1540s cm.$^{-1}$ (Found: C, 60·6; H, 9·1; N, 14·1. C_5H_9NO requires C, 60·6; H, 9·15; N, 13·75%).

Cyclobutyl isocyanide. Cyclobutylformamide (8·0 g., 0·08 mole) was converted into cyclobutyl isocyanide as above. The reaction temperature was 50°, and the system was maintained at 5—10 mm. The colourless *isocyanide* which collected in a liquid-nitrogen-cooled receiver in 40 min. was transferred twice by high-vacuum procedures, to separate it from a small amount of quinoline. The product (1·6 g., 24%) was completely homogeneous (gas–liquid chromatography; (di-isodecyl phthalate on diatomaceous earth; 2 m.; 86°; retention volume, 2230 c.c. of helium) (Found: C, 74·0; H, 8·4; N, 17·6. C_5H_7N requires C, 74·0; H, 8·7; N, 17·3%). It had $\nu_{max.}$ 2137 cm.$^{-1}$ (100 mm.; gas; 16 mm.). The proton resonance spectrum of cyclobutyl isocyanide (tetramethylsilane as internal standard) was composed of a quintet centered at 3·99 p.p.m. and a very complex multiplet centered at 2·07 p.p.m., in the area ratio of 1 : 6, which is consistent with the proposed structure. No proton absorption was detected at less than 1·0 p.p.m., indicating the absence of cyclopropylcarbinyl derivatives.

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* The simple expedient of employing toluene-*p*-sulphonic acid as a catalyst represents a noteworthy improvement over existing methods of synthesis.[11]

[8] Williams, *J. Chem. Phys.*, 1956, **25**, 224, 235.
[9] Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen and Company, Ltd., London, 2nd edn., 1958, p. 265.
[10] Logemann, Artini, and Tosolini, *Chem. Ber.*, 1958, **91**, 2566.
[11] See, *e.g.*, Ritter and Kalish, *J. Amer. Chem. Soc.*, 1948, **70**, 4048; Moffat, Newton, and Papenmeier, *J. Org. Chem.*, 1962, **27**, 4058.
[12] Iffland, Criner, Koral, Lotspeich, Papanastassion, and White, *J. Amer. Chem. Soc.*, 1953, **75**, 4044.

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817. *Aromatic Polyfluoro-compounds. Part XIV.*[1] *Phenylation of Hexafluorobenzene and Some Replacement Reactions of* 2,3,4,5,6-*Pentafluorobiphenyl.*

By M. T. Chaudhry and R. Stephens.

When phenyl-lithium in diethyl ether was added to hexafluorobenzene in the same solvent a vigorous reaction occurred, as noted by others,[2] and 2,3,4,5,6-pentafluorobiphenyl (I) and 2′,3′,5′,6′-tetrafluoro-*p*-terphenyl (II) were formed. This nucleophilic attack on hexafluorobenzene provides another example of *para*-orientation in the second substitution.[1,3] The identity of the tetrafluoroterphenyl was established by its formation in

[1] Part XIII, Robson, Smith, Stephens, and Tatlow, *J.*, 1963, 3692.
[2] Antonucci and Wall, 140th Meeting Amer. Chem. Soc., Sept. 3rd, 1961, 25M.
[3] Brooke, Burdon, Stacey, and Tatlow, *J.*, 1960, 1768; Robson, Stacey, Stephens, and Tatlow, *J.*, 1960, 4754; Alsop, Burdon, and Tatlow, *J.*, 1962, 1801; Tatlow, *Endeavour*, 1963, **22**, 89.

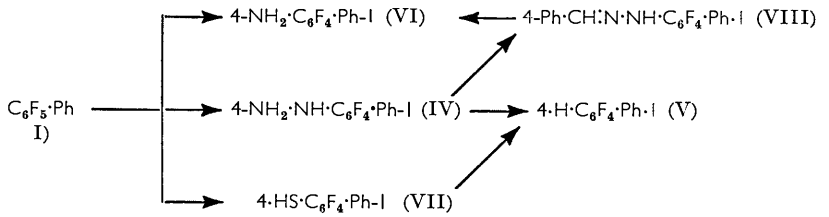
an Ullmann reaction involving bromobenzene and 1,4-dibromotetrafluorobenzene (III). The product (II) has a high melting point and low solubility characteristic of *p*-terphenyls.

$$C_6F_6 \longrightarrow C_6F_5\cdot Ph\ (I) \longrightarrow 1\text{-}Ph\cdot C_6F_4\cdot Ph\text{-}4\ (II) \longleftarrow 2PhBr + 1\text{-}Br\cdot C_6F_4\cdot Br\text{-}4\ (III)$$

As then expected, 2,3,4,5,6-pentafluorobiphenyl readily reacted with other nucleophilic reagents, *viz.*, hydrazine, ammonia, and sodium hydrogen sulphide, to give products in which the fluorine atom *para* to the phenyl group had been replaced.[1,3] This was established by nuclear magnetic resonance spectroscopy on two compounds, (V) and (VII), which had solubilities sufficiently high for this technique.

Reaction of 2,3,4,5,6-pentafluorobiphenyl with hydrazine gave 2,3,5,6-tetrafluoro-4-hydrazinobiphenyl (IV) which was characterised as the hydrochloride and as a hydrazone with benzaldehyde. The orientation was established by removal of the hydrazine group with Fehling's solution to give 2,3,5,6-tetrafluorobiphenyl (V) whose nuclear magnetic resonance spectrum showed only the two expected magnetically different kinds of fluorine atoms; the two isomers should display four.

When the benzaldehyde hydrazone (VIII) was reduced with zinc dust in acetic acid, 4-amino-2,3,5,6-tetrafluorobiphenyl (VI) was produced and this was also obtained from 2,3,4,5,6-pentafluorobiphenyl and aqueous ammonia at 160°.



2,3,5,6-Tetrafluoro-4-mercaptobiphenyl (VII) was prepared from pentafluorobiphenyl (I) and sodium hydrogen sulphide in dimethylformamide.[1] Its structure was established by nuclear magnetic resonance spectroscopy which revealed only two magnetically different kinds of fluorine and by desulphurisation with Raney nickel [1] in ethanol to 2,3,5,6-tetrafluorobiphenyl (V), also obtained from the hydrazine (IV).

Experimental

Phenylation of Hexafluorobenzene.—Phenyl-lithium (6·4 g.) in ether (60 c.c.) was added dropwise to hexafluorobenzene (13·2 g.) in ether (40 c.c.) at a rate sufficient to maintain a gentle reflux. The mixture was then stirred for 3 hr., water (200 c.c.) added, and the ether layer separated, dried ($MgSO_4$), filtered, and evaporated to leave a light brown solid which was sublimed and recrystallised from light petroleum (b. p. 60—80°) to give 2,3,4,5,6-pentafluorobiphenyl (I) (6·3 g.), m. p. 110—112° (lit.,[4] 111—112°) (Found: C, 58·8; H, 2·2. Calc. for $C_{12}H_5F_5$: C, 59·0; H, 2·0%), $\lambda_{max.}$ 2725 Å (ε 7·6 × 10^3) in EtOH. The aqueous layer and the precipitate were extracted continuously with ether for 96 hr. The crystals (1·8 g.), m. p. 258—259°, which separated from the boiling ether were identical (infrared spectroscopy) with the residue (0·2 g.), m. p. 258—259°, left on evaporation of the filtered ether solution, and sublimation gave 2′,3′,5′,6′-*tetrafluoro*-p-*terphenyl* (II), m. p. 259—260° (Found: C, 71·7; H, 3·6. $C_{18}H_{10}F_4$ requires C, 71·5; H, 3·3%). The water-insoluble residue left after the continuous ether-extraction was sublimed at 180°/0·2 mm., to give a further quantity of this compound (1·2 g.), m. p. 260°.

2′,3′,5′,6′-*Tetrafluoro*-p-*terphenyl.*—1,4-Dibromotetrafluorobenzene (III) (3·0 g.), bromobenzene (6·0 g.), and copper bronze (10 g.) were kept in a sealed tube at 200° for 24 hr. The ether-insoluble product sublimed to give 2′,3′,5′,6′-tetrafluoro-*p*-terphenyl (II) (0·5 g.), m. p. and mixed m. p. 259—260° (infrared spectrum as for the above terphenyl).

2,3,5,6-*Tetrafluoro*-4-*hydrazinobiphenyl.*—2,3,4,5,6-Pentafluorobiphenyl (I) (2·0 g.), 100% w/w hydrazine hydrate (6 c.c.), ethanol (12 c.c.), and water (6 c.c.) were refluxed together for

[4] Birchall, Haszeldine, and Parkinson, *J.*, 1962, 4966.

12 hr., cooled, diluted with water (25 c.c.), and continuously extracted with methylene chloride for 16 hr. The dried ($MgSO_4$) extract was filtered and evaporated to leave a brown solid (1·1 g.) which on recrystallisation from ethanol gave 2,3,5,6-*tetrafluoro*-4-*hydrazinobiphenyl* (IV) (0·9 g.), m. p. 139—140° (Found: C, 56·3; H, 3·2. $C_{12}H_8F_4N_2$ requires C, 56·3; H, 3·1%), $\lambda_{max.}$ 2755 Å (ε 4·2 × 10^4) in EtOH, $\nu_{max.}$ (in Nujol) 3300, 3200, 1570, and 1560 (NH), 1640, 1610, and 1500 (fluorinated aromatic nucleus), 720 and 690 $cm.^{-1}$ (Ph).

2,3,5,6-Tetrafluoro-4-hydrazinobiphenyl (0·2 g.), ethanol (3 c.c.), and benzaldehyde (1 c.c.) were refluxed for 10 min., then cooled, and the precipitate was collected and recrystallised from ethanol to give the *hydrazone* (VIII) (0·25 g.), m. p. 210—211° (Found: C, 66·6; H, 3·5. $C_{19}H_{12}F_4N_2$ requires C, 66·3; H, 3·5%).

Dry hydrogen chloride was bubbled through 2,3,5,6-tetrafluoro-4-hydrazinobiphenyl (0·5 g.) in dry ether (10 c.c.) for ½ hr. to give its *hydrochloride* (0·4 g.), m. p. 245—246° (Found: C, 49·3; H, 3·3. $C_{12}H_9ClF_4N_2$ requires C, 49·2; H, 3·1%).

4-*Amino*-2,3,5,6-*tetrafluorobiphenyl*.—(i) The hydrazone (VIII) (2·5 g.), zinc dust (5·0 g.), and acetic acid (30 c.c.) were refluxed for 3 hr., diluted with 10N-sulphuric acid, and steam-distilled to give crystals which recrystallised from light petroleum (b. p. 60—80°) to give 4-amino-2,3,5,6-tetrafluorobiphenyl (VI) (0·5 g.), m. p. 90—91° alone and in admixture with the amine recorded below, $\lambda_{max.}$ 2625 Å (ε 1·95 × 10^4) in EtOH. (ii) 2,3,4,5,6-Pentafluorobiphenyl (I) (2·0 g.), aqueous ammonia (*d* 0·88; 6 c.c.), and ethanol (10 c.c.) were kept at 160° for 16 hr. The product was diluted with water, then extracted with methylene chloride for 16 hr., and the extract was dried ($MgSO_4$), filtered, and evaporated to leave a solid (1·8 g.) which on two recrystallisations from light petroleum (b. p. 60—80°) gave the *amine* (1·4 g.), m. p. 86—88° (Found: C, 59·5; H, 2·8. $C_{12}H_7F_4N$ requires C, 59·7; H, 2·9%). Both specimens had the same infrared spectrum with $\nu_{max.}$ 3250 and 3350 (NH), 1650 and 1505 (fluorinated aromatic ring) and at 720 and 690 $cm.^{-1}$ (Ph).

The amine (0·5 g.), acetic anhydride (1 c.c.), and concentrated sulphuric acid (0·1 c.c.) were refluxed for 15 min., affording the *acetyl derivative* (0·3 g.), m. p. 125—126° (from aqueous methanol) (Found: C, 59·6; H, 3·1. $C_{14}H_9F_4NO$ requires C, 59·4; H, 3·2%).

2,3,5,6-*Tetrafluorobiphenyl*.—2,3,5,6-Tetrafluoro-4-hydrazinobiphenyl (IV) (6·0 g.) and Fehling's solution (300 c.c. each of solutions "A" and "B") were refluxed together for 1 hr., a red precipitate was formed, and crystals were deposited in the condenser. The remainder of the product was distilled from the reaction mixture in steam, and the whole (4·0 g.) recrystallised from light petroleum (b. p. 60—80°), to give 2,3,5,6-*tetrafluorobiphenyl* (V) (3·1 g.), m. p. 103—105° (Found: C, 64·0; H, 2·7. $C_{12}H_6F_4$ requires C, 63·7; H, 2·7%), $\lambda_{max.}$ 2400 Å (ε, 8·3 × 10^3) in EtOH, $\nu_{max.}$ 3050 (·CH:), 1625 and 1495 (fluorinated aromatic), 715 and 695 $cm.^{-1}$ (Ph). The ^{19}F nuclear magnetic resonance spectrum of a M-solution of this compound in acetone has two multiplets of equal intensity.

2,3,5,6-*Tetrafluoro*-4-*mercaptobiphenyl*.—2,3,4,5,6-Pentafluorobiphenyl (I) (12·0 g.) in dimethylformamide (30 c.c.) was added to a stirred suspension of sodium hydrogen sulphide (45 g.) in dimethylformamide (85 c.c.). When the initial reaction had subsided the mixture was kept at 110° for 5 min., then added to ice–water (300 c.c.), acidified with 8N-hydrochloric acid, and extracted with ether. The dried ($MgSO_4$) extract was evaporated to a pale brown solid (11·0 g.), m. p. 75—89°, which recrystallised twice from alcohol to give 2,3,5,6-*tetrafluoro*-4-*mercaptobiphenyl* (VII) (8·0 g.), m. p. 118—120° (Found: C, 56·0; H, 2·0. $C_{12}H_6F_4S$ requires C, 55·8; H, 2·3%), $\lambda_{max.}$ 2675 Å (ε 2·8 × 10^4) in EtOH, $\nu_{max.}$ 3050 (·CH:), 2600vw (SH), and 1630, 1580, 1495, and 1480 $cm.^{-1}$ (fluorinated aromatic). The ^{19}F nuclear magnetic resonance spectrum of a M-solution in acetone has two multiplets of equal intensity.

This thiol (3·3 g.) was added to a suspension of Raney nickel (grade W 4; 25 g.) in ethanol. When the initial reaction had subsided the mixture was refluxed for 2 hr. and then filtered. The solid residue obtained on evaporation recrystallised from light petroleum (b. p. 60—80°) to give 2,3,5,6-tetrafluorobiphenyl (V) (1·6 g.), m. p. 103—104° alone and in admixture with the previously described tetrafluorobiphenyl; the infrared spectrum was correct.

We thank Professor J. C. Tatlow for his interest, Dr. L. F. Thomas for the magnetic measurements, Miss D. M. Bick for experimental assistance, and the West Pakistan Education Department and the British Council for scholarship awards (to M. T. C.).

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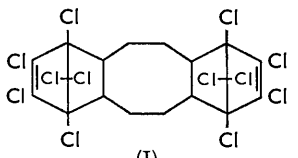
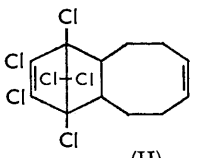
818. *Adducts of Hexachlorocyclopentadiene with Cyclo-octa-1,5-diene and Cyclohepta-1,3,5-triene.*

By G. I. Fray.

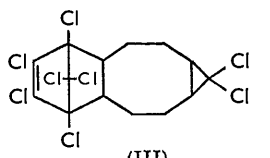
It has been reported that the Diels–Alder addition of hexachlorocyclopentadiene to *cis,cis*-cyclo-octa-1,5-diene takes place very readily, with the formation of the 2 : 1-adduct (I).[1] It was of interest to prepare the hitherto unknown 1 : 1-adduct (II) and certain of its derivatives in view of their structural relationship to the aldrin–dieldrin group of insecticides. The 1 : 1-adduct was obtained in good yield by using a large excess of cyclo-octadiene; it formed a dihydro-, a dichloro-, a dibromo-, and an epoxy-derivative, and further reaction with hexachlorocyclopentadiene furnished the known 2 : 1-adduct (I). In addition, the tetracyclic compound (III) was formed, in low yield, by the action of dichlorocarbene (from sodium trichloroacetate [2]) on (II). Reaction of dichlorocarbene with cyclo-octadiene itself afforded the 1 : 1-adduct (IV) together with a little of the 2 : 1-adduct (V).



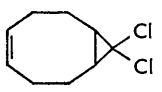
(I)



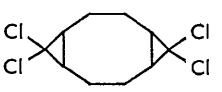
(II)



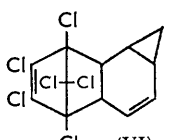
(III)



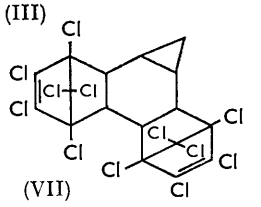
(IV)



(V)



(VI)



(VII)

For comparison with the above adducts, the 1 : 1- and the 2 : 1-adduct of hexachlorocyclopentadiene with cyclohepta-1,3,5-triene were prepared. In view of the well-established tendency of the cycloheptatriene ring system to react as bicyclo[4,1,0]hepta-2,4-diene,[3] the adducts were formulated as (VI) and (VII), respectively. The 1 : 1-adduct (VI) took up two molecules of hydrogen to yield a tetrahydro-derivative (possibly a mixture of isomers), but bromination with an excess of bromine in cold chloroform afforded a dibromo-derivative only; the 2 : 1-adduct (VII) was not affected by bromine under these conditions. These experiments confirmed the structures assigned to the two adducts.

Experimental.—Unless stated otherwise, light petroleum refers to the fraction of b. p. 40—60°. Hydrogenations were carried out at atmospheric pressure in the presence of 2% palladised strontium carbonate. Reactions with chlorine and bromine were carried out in cold chloroform.

1,10,11,12,13,13-*Hexachlorotricyclo*[8,2,1,$0^{2,9}$]*trideca*-5,11-*diene* (II). A mixture of hexachlorocyclopentadiene (17 g.) and cyclo-octadiene (56 g.) was refluxed gently for 1 hr. Fractional distillation then afforded the 1 : 1-*adduct* (18 g., 76%), b. p. 153—158°/0·5 mm., obtained as prisms, m. p. 66—67° (from methanol–light petroleum) (Found: C, 40·8; H, 3·0; Cl, 56·2. $C_{13}H_{12}Cl_6$ requires C, 41·0; H, 3·2; Cl, 55·8%).

The dihydro-derivative was obtained from methanol as plates, m. p. 86·5—87·5° (lit.,[1] m. p. 82—84°) (Found: C, 40·6; H, 4·0; Cl, 55·5. Calc. for $C_{13}H_{14}Cl_6$: C, 40·8; H, 3·7; Cl, 55·5%). The *dichloro-derivative* formed prisms, m. p. 165—166·5° (from acetone) (Found: C, 34·7; H, 2·9; Cl, 62·3. $C_{13}H_{12}Cl_8$ requires C, 34·5; H, 2·7; Cl, 62·8%). The *dibromo-derivative* formed prisms, m. p. 200—201° (from chloroform) (Found: C, 29·1; H, 2·3; Hal, 68·8. $C_{13}H_{12}Br_2Cl_6$ requires C, 28·9; H, 2·2; Hal, 68·9%). The *epoxy-derivative* (prepared with perbenzoic acid in

[1] Ziegler and Froitzheim-Kühlhorn, *Annalen*, 1954, **589**, 157.
[2] Wagner, *Proc. Chem. Soc.*, 1959, 229.
[3] Alder and Jacobs, *Chem. Ber.*, 1953, **86**, 1528; and later papers.

chloroform) formed plates, m. p. 135—136° (from methanol) (Found: C, 39·5; H, 3·3; Cl, 53·7. $C_{13}H_{12}Cl_6O$ requires C, 39·3; H, 3·0; Cl, 53·6%).

The above 1 : 1-adduct reacted with hexachlorocyclopentadiene to yield the 2 : 1-adduct as prisms, m. p. >360° (from chlorobenzene) (cf. ref. 1) (Found: C, 33·4; H, 1·9; Cl, 64·7. Calc. for $C_{18}H_{12}Cl_{12}$: C, 33·1; H, 1·8; Cl, 65·1%).

1,6,6,11,12,13,14,14-*Octachlorotetracyclo*[9,2,1,$0^{2,10}$,$0^{5,7}$]*tetradec*-12-*ene* (III). A mixture of the above 1 : 1-adduct (14 g.), sodium trichloroacetate (14 g.), and 1,2-dimethoxyethane (50 c.c.) was refluxed for 2 hr. The resulting dark mixture was filtered and the filtrate evaporated. Treatment of the residue with methanol–acetone afforded the *product* as plates (1·6 g., 9%), m. p. 234·5—235·5° (from light petroleum, b. p. 60—80°; charcoal) (Found: C, 36·1; H, 2·6; Cl, 61·5. $C_{14}H_{12}Cl_8$ requires C, 36·2; H, 2·6; Cl, 61·2%).

9,9-*Dichlorobicyclo*[6,1,0]*non*-4-*ene* (IV) *and* 5,5,10,10-*tetrachlorotricyclo*[7,1,0,$0^{4,6}$]*decane* (V). A mixture of cyclo-octadiene (50 g.), sodium trichloroacetate (18 g.), and 1,2-dimethoxyethane (35 c.c.) was kept at 100—110° (bath) for 16 hr. Filtration, followed by fractional distillation of the filtrate, afforded *compound* (IV) as an oil (11 g., 59%), b. p. 111—114°/13 mm., $n_D^{20.5}$ 1·5243 (Found: C, 56·5; H, 6·4; Cl, 37·1. $C_9H_{12}Cl_2$ requires C, 56·6; H, 6·3; Cl, 37·1%). The *dibromo-derivative* was obtained as prisms, m. p. 70·5° (from methanol) (Found: C, 31·0; H, 3·5; Hal, 65·5. $C_9H_{12}Br_2Cl_2$ requires C, 30·8; H, 3·4; Hal, 65·7%).

The residue from the above distillation crystallised on cooling. Recrystallisation from methanol–acetone (charcoal) furnished *compound* (V) as needles (0·35 g.), m. p. 174·5—175·5° (Found: C, 43·8; H, 4·2; Cl, 52·1. $C_{10}H_{12}Cl_4$ requires C, 43·8; H, 4·4; Cl, 51·7%).

1,9,10,11,12,12-*Hexachlorotetracyclo*[7,2,1,$0^{2,8}$,$0^{5,7}$]*dodeca*-3,10-*diene* (VI). A mixture of hexachlorocyclopentadiene (8·5 g.) and cycloheptatriene (25 g.) was kept at 120—130° (bath) for 16 hr. Fractional distillation then yielded the 1 : 1-*adduct* (9·4 g., 83%), b. p. 140—144°/0·2 mm., which formed prisms, m. p. 93·5—94·5° (from methanol) (Found: C, 39·5; H, 2·4; Cl, 58·3. $C_{12}H_8Cl_6$ requires C, 39·5; H, 2·2; Cl, 58·3%). Hydrogenation afforded the *tetrahydro-derivative*, which formed plates, m. p. 76·5—77·5° (from methanol) (Found: C, 39·1; H, 3·6; Cl, 57·6. $C_{12}H_{12}Cl_6$ requires C, 39·1; H, 3·3; Cl, 57·6%). This was possibly a mixture of isomers; the adduct from hexachlorocyclopentadiene and cycloheptene had m. p. 78—80°.[1] The *dibromo-derivative* formed needles, m. p. 144·5—145·5° (from methanol) (Found: C, 27·7; H, 1·6; Hal, 70·7. $C_{12}H_8Br_2Cl_6$ requires C, 27·5; H, 1·5; Hal, 71·0%).

1,7,8,9,10,13,14,15,16,16,17,17-*Dodecachlorohexacyclo*[11,2,1,$1^{7,10}$,$0^{2,12}$,$0^{3,5}$,$0^{6,11}$]*heptadeca*-8,14-*diene* (VII). A mixture of hexachlorocyclopentadiene (11 g.) and cycloheptatriene (1·1 g.) was kept at 150—160° (bath) for 16 hr. The resulting crystalline mass was washed with ether–methanol to afford the 2 : 1-*adduct* (4·3 g., 56%), which formed needles, m. p. 302—303° (decomp.) (from butan-1-ol; charcoal) (Found: C, 31·7; H, 1·5; Cl, 66·9. $C_{17}H_8Cl_{12}$ requires C, 32·0; H, 1·3; Cl, 66·7%).

The author thanks Sir Robert Robinson, who suggested this work, for his interest and advice.

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819. *The Instability of Co-ordination Compounds of Silicon Tetrachloride in Solution.*

By I. R. BEATTIE and M. WEBSTER.

WITH the exception of silicon tetrafluoride, compounds of silicon do not appear to form adducts which are stable in solution. Eaborn [1] found that the ultraviolet absorption spectra of *p*-toluidine and pyridine were the same in several organosilicon solvents as

[1] Eaborn, *J.*, 1955, 2047.

they were in hexane. He subsequently pointed out [2] that these weakly polar solvents are not conducive to co-ordination. Addition compounds of silicon tetrachloride are usually intractable solids, insoluble in solvents with which they do not react, although at elevated temperatures they may dissolve in an excess of the ligand.

Issleib and Reinhold [3] have recently reported that the 1 : 2 adduct of silicon tetrachloride with tricyclohexylphosphine is soluble in benzene, with a molecular weight (determined cryoscopically) of 717·5 compared with a theoretical value of 730·3 for the undissociated monomer $SiCl_4,2(C_6H_{11})_3P$. In view of the importance of this compound for studying the acceptor strength of silicon tetrachloride, we have repeated this work. We find that silicon tetrachloride does not react with tricyclohexylphosphine under anhydrous conditions in the absence of oxygen. A molecular-weight determination in benzene on the constituents mixed in the correct ratio for a 1 : 2 adduct showed complete dissociation. However, passage of hydrogen chloride into a benzene solution of tricyclohexylphosphine, followed by removal of the solvent, left a compound soluble in benzene and containing P–H bonds. It appears possible that this was the compound obtained by Issleib and Reinhold. The lack of reaction of silicon tetrachloride with tricyclohexylphosphine is in agreement with its lack of reaction with *o*-phenylenebisdimethylarsine.[4]

Unstable compounds of silicon tetrachloride, for example $SiCl_4,NMe_3$,[5] which has a vapour pressure of 6 mm. at −54°, could be regarded as being soluble in organic solvents. However, it is more reasonable to suppose that such adducts are fully dissociated in solution at room temperature. The compound formed by treating silicon tetrachloride with *NNN'N'*-tetramethylethylenediamine (TMEN) represents a reasonably stable 1 : 1 addition compound [6] (dissociation pressure of 6 mm. at 18°) which is so soluble that Schnell and Wersin [7] reported no adduct formation when solutions of the reagents in benzene were mixed. We have examined the infrared spectrum of the 1 : 1 addition compound of silicon tetrachloride with this diamine in the solid state and in solution in benzene. In the rock-salt region the spectrum of the solid closely resembles that of the corresponding 1 : 1 addition compound of tin tetrachloride.[8] In the cæsium bromide region, apart from weak ligand vibrations, there are only three strong bands, at 400, 435, and 474 $cm.^{-1}$, attributable to silicon–chlorine stretching vibrations and characteristic of a *cis*(chelate)-adduct.[8,9] In solution in benzene there are no vibrations attributable to these modes in the region 580—250 $cm.^{-1}$, indicating that the compound is highly dissociated. Further, the spectrum of free silicon tetrachloride was observed for these solutions.

The similarity of the spectra of the MCl_4,TMEN adducts in the near-infrared region (where M = Si or Sn) suggests that both nitrogen atoms are involved in co-ordination. Further, the positions of the M–Cl vibrations in both of these compounds are in the region to be expected for octahedral co-ordination in a complex MCl_4L_2 (where L = monodentate ligand or L_2 = bidentate ligand).[8-10] No 1 : 2 adduct of silicon tetrachloride with trimethylamine is known, and with triethylamine no adduct formation occurs at all. The production of small quantities of triethylammonium chloride has been reported [6] from the reaction of triethylamine with silicon tetrachloride in a vacuum-system. However, we find that these two reagents can be left in contact for several weeks without apparent reaction. Thus the occurrence of a relatively stable 1 : 1 adduct $SiCl_4$,TMEN with *bridging* diamine is extremely unlikely. Our observations of the M–Cl stretching vibrations in this compound can be completely rationalised in terms of a chelate adduct.

[2] Eaborn, " Organosilicon Compounds," Butterworths, London, 1960.
[3] Issleib and Reinhold, *Z. anorg. Chem.*, 1962, **314**, 113.
[4] Clark, Lewis, and Nyholm, *J.*, 1962, 2460.
[5] Burg, *J. Amer. Chem. Soc.*, 1954, **76**, 2674.
[6] Fergusson, Grant, Hickford, and Wilkins, *J.*, 1959, 99.
[7] Schnell and Wersin, *Monatsh.*, 1961, **92**, 1055.
[8] Beattie and Rule, unpublished observations.
[9] Beattie, McQuillan, Rule, and Webster, *J.*, 1963, 1514.
[10] Beattie and Gilson, unpublished observations.

Experimental.—Preparation of reagents. Silicon tetrachloride and triethylamine were purified as described previously; [11,12] *NNN'N'*-tetramethylethylenediamine was refluxed over calcium hydride for 3 days, distilled on to fresh calcium hydride, and distilled *in vacuo* into ampoules; benzene and carbon tetrachloride were dried over calcium hydride; tricyclohexylphosphine was prepared by Issleib and Brack's method [13] and was isolated as the carbon disulphide adduct, m. p. (sealed tube) 106—120° (lit., 118°,[13] 115—117° [14]) (Found: C, 64·15; H, 9·3: P, 8·9; S, 17·7. Calc. for $C_{19}H_{33}PS_2$: C, 64·0; H, 9·3; P, 8·7%; S, 18·0). Sublimation of the brick-red carbon disulphide adduct yielded the white phosphine, m. p. 84° (lit., 76—78°,[13] 74—76° [14]) (Found: C, 77·0; H, 11·5; P, 11·6. Calc. for $C_{18}H_{33}P$: C, 77·1; H, 11·9; P, 11·05%).

The system $SiCl_4$,$(C_6H_{11})_3P$. (*a*) *Dry-box experiments.* Oxygen was removed by flushing with nitrogen, followed by continuous circulation over heated copper and copper oxide.[15] A solution of tricyclohexylphosphine in carbon tetrachloride, on treatment with silicon tetrachloride, gave no precipitate. A similar reaction in benzene with approximately the same quantities of reagents as were used by Issleib and Reinhold [3] likewise gave no precipitate. Removal of the volatile materials left a white solid which was shown by infrared spectroscopy to be a mixture of silica, tricyclohexylphosphine, and a small amount of another material.

Bubbling dry hydrogen chloride into a benzene solution of tricyclohexylphosphine left a clear solution. Removal of the volatile materials left a white substance (C, 61·2; H, 10·2; Cl, 16·4. Calc. for $C_{18}H_{34}PCl$: C, 68·2; H, 10·8; Cl, 11·2%), whose infrared spectrum contained a broad band at 2370 $cm.^{-1}$, assigned to a P–H vibration. There was a further intense band at 700—1000 $cm.^{-1}$.

(*b*) *Vacuum experiments.* An all-glass system was used, including a magnetically stirred cryoscope with a 10-junction copper–constantan thermocouple. The freezing points of benzene, a solution of tricyclohexylphosphine (0·1822 g.) in benzene (7·872 g.), and a solution of tricyclohexylphosphine (0·1822 g.) and silicon tetrachloride (0·0642 g.) in benzene (7·872 g.) were determined. The molecular weight of tricyclohexylphosphine was found to be 263 (calc. 280). Addition of silicon tetrachloride increased the depression. The depression calculated for the tricyclohexylphosphine–silicon tetrachloride solution in benzene for no adduct formation was 0·664° whereas that calculated for the formation of $SiCl_4,2(C_6H_{11})_3P$ was 0·244°. The observed depression was 0·643°.

The system $SiCl_4$–$(CH_2{\cdot}NMe_2)_2$. An excess of the diamine was distilled on to solid silicon tetrachloride in an all-glass vacuum-system. On allowing the mixture to warm, a white solid remained. After removal of the excess amine the infrared spectrum of this solid was examined at about 80°K. When the adduct was sublimed on to a cooled plate, initial spectra showed the presence of free silicon tetrachloride (ν_3 603 $cm.^{-1}$), but on allowing the plate to warm to room temperature and then cooling again, this band disappeared. The solution spectrum in benzene was taken in a vacuum-cell.

The system $SiCl_4$–NEt_3. Silicon tetrachloride (~3 g.) was distilled on to solid triethylamine (~1·6 g.) in an all-glass vacuum-system and allowed to warm. 14 mg. of solid were formed. The volatile materials were removed and left for several weeks without apparent further reaction.

The infrared spectra were recorded on a Perkin-Elmer 221 spectrophotometer equipped with rock-salt grating, and cæsium bromide optics.

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Department of Chemistry, King's College (University of London),
Strand, London, W.C.2. [*Received, March 25th*, 1963.]

[11] Beattie and Leigh, *J. Inorg. Nuclear Chem.*, 1961, **23**, 55.
[12] Beattie and Webster, *J.*, 1961, 1730.
[13] Issleib and Brack, *Z. anorg. Chem.*, 1954, **277**, 258.
[14] Oppegard, U.S.P. 2,687,437/1954 (*Chem. Abs.*, 1955, **49**, 11,000i).
[15] Dodd and Robinson, "Experimental Inorganic Chemistry," Elsevier Publ. Co., Amsterdam, 1957, p. 167.

820. *Studies with Dithizone. Part XI.*[1] *Reactions with* p-*Fluorophenyl- and* p-*Iodophenyl-mercury*(II) *Compounds.*

By H. Irving and A. M. Kiwan.

The statement[1] that *p*-fluorophenylmercury(II) acetate and *p*-iodophenylmercury(II) chloride react with a solution of dithizone in carbon tetrachloride to give mercury(II) dithizonate has been re-investigated and found to be incorrect.

By using freshly synthesised specimens of these compounds and a spectrophotometric procedure adapted to two-phase systems,[2] it is found that in each case a 1 : 1 complex is formed which can be quantitatively extracted from aqueous solutions covering a wide range of pH values to give a yellow solution in the organic phase with $\lambda_{max.} = 478$ ($10^{-3}\ \varepsilon = 36{\cdot}0 \pm 0{\cdot}6$) and $\lambda_{max.} = 477$ ($10^{-3}\ \varepsilon = 34{\cdot}8 \pm 0{\cdot}3$), respectively. This behaviour is exactly comparable to that of *p*-chloro- and *p*-bromo-phenylmercury(II) salts,[1] and statements in Part X [1] (p. 468, last 10 lines; p. 472, second paragraph) should be corrected.

Experimental.—p-Fluorophenylmercury(II) *chloride.* This compound was prepared by heating fluorobenzene (10 g.) with mercuric acetate (3·0 g.) and glacial acetic acid (3 ml.) under reflux (2 hr.). Hot 50% aqueous ethanol (50 ml.) was then added and the mixture filtered while hot. Sodium chloride (excess) in aqueous alcohol was added to the filtrate and the precipitate of *p*-fluorophenylmercury(II) chloride was collected from the hot solution and recrystallised from benzene. The *salt* (1·5 g.) had m. p. 277° (Found: F, 6·0; Hg 60·6. C_6H_4ClFHg requires F, 5·7; Hg, 60·6%).

Extractive titration of 5 ml. of a $2{\cdot}63 \times 10^{-5}$ M-solution of dithizone in carbon tetrachloride with 5 ml. of an acetate buffer of pH 3·95, with x ml. of a $2{\cdot}65 \times 10^{-5}$ M-solution of *p*-fluorophenylmercury(II) chloride, and $(10 - x)$ ml. of water gave the following optical-density readings (1 cm. cell):

x (ml.)	0·0	1·0	2·0	3·0	4·0	4·5	5·0	5·5	6·0	7·0	8·0
A at 478 mμ	0·402	0·512	0·618	0·734	0·837	0·892	0·920	0·938	0·958	0·958	0·954
A at 620 mμ	0·900	0·711	0·522	0·362	0·200	0·104	0·049	0·023	0·004	0·004	0·008

The equivalent point occurred when $x = 5{\cdot}0$ ml., whence the molar ratio, *p*-fluorophenylmercury(II) : dithizone = 1·00 : 0·992.

The percentage of this 1 : 1 complex extracted into carbon tetrachloride varied slightly with pH as shown by the following results:

pH	1·35	1·83	3·04	3·72	4·74	6·42	7·61	9·64	10·63	12·02
Extraction (%)	96·9	99·5	98·6	99·1	98·5	98·9	100·0	96·6	95·6	93·7

p-*Iodophenylmercury*(II) *chloride.*—This was prepared by the direct mercuration of iodobenzene.[3] It was recrystallised from benzene and had m. p. 287° (Found: Hg, 45·4. Calc. for C_6H_4ClIHg; Hg, 45·7%).

Extractive titration of 5 ml. of a $3{\cdot}225 \times 10^{-5}$ M-solution of dithizone in chloroform by 5 ml. of an acetate buffer of pH 4, with x ml. of $3{\cdot}0 \times 10^{-5}$ M-solution of *p*-iodophenylmercuric chloride in chloroform and $(10 - x)$ ml. of chloroform gave the following results:

x (ml.)	0·0	1·0	2·0	3·0	4·0	4·5	5·0	5·5	6·0	8·0
A at 477 mμ	0·126	0·164	0·213	0·263	0·310	0·334	0·357	0·370	0·370	0·369
A at 605 mμ	0·445	0·365	0·268	0·187	0·105	0·056	0·021	0·002	0·001	0·001

The equivalent point occurred when $x = 5{\cdot}3$, whence the molar ratio *p*-iodophenylmercury(II) : dithizone = 1·01 : 1·00. The percentage of *p*-iodophenylmercury(II) dithizonate extracted at various pH values is given by:

pH	0·83	1·33	2·23	3·40	4·62	6·14	6·79	7·38	8·29	9·30	10·21	12·20
Extraction (%)	95·8	97·8	99·4	98·8	100·6	100·0	99·4	100·0	98·9	100·6	100·0	99·4

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[1] Part X, Irving and Cox, *J.*, 1963, 466.
[2] Irving and Cox, *J.*, 1961, 1470.
[3] Nesmejanow, *Ber.*, 1929, **62**, 1010.