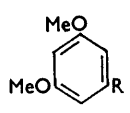
NOTES.

386. *Studies in Mycological Chemistry. Part X.* Synthesis of Flaviolin (2,5,7-Trihydroxy-1,4-naphthaquinone).*

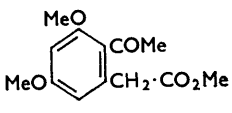
By B. W. Bycroft and John C. Roberts.

Flaviolin (IVb), a metabolite of *Aspergillus citricus* (Wehmer) Mosseray,[1] has not been synthesized hitherto. Its structure has been derived from degradative evidence [1] and established by synthesis [2,3] of its tri-*O*-methyl ether. We now describe a novel and efficient synthesis of the 5,7-di-*O*-methyl ether (IVa) and its demethylation, in poor yield, to flaviolin.

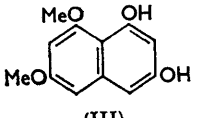
2-Hydroxy-5,7-dimethoxy-1,4-naphthaquinone was synthesized in the following way. 3,5-Dimethoxybenzoyl chloride (Ia) was converted, by a modification [4] of the Arndt–Eistert method, into methyl 3,5-dimethoxyphenylacetate (Ib). Acetylation [5] of this compound yielded the ester-ketone (II) which readily cyclised,[6] under the action of base,



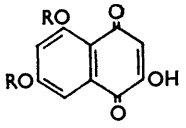
(Ia : R = COCl)
(Ib : R = $CH_2 \cdot CO_2Me$)



(II)



(III)



(IVa : R = Me)
(IVb : R = H)

to give 1,3-dihydroxy-6,8-dimethoxynaphthalene (III). This substance, which was not isolated, underwent aerial oxidation,[3,6] in presence of alkali, to yield the desired product (IVa). Methylation of compound (IVa) gave 2,5,7-trimethoxy-1,4-naphthaquinone (tri-*O*-methylflaviolin). Demethylation of compound (IVa) was accompanied by extensive degradation and gave flaviolin (IVb) in a yield of only 1·3%.

Experimental.—M. p.s were determined on the Kofler block. Ultraviolet absorption spectra were measured on ethanolic solutions with a Unicam SP. 700 spectrophotometer. Infrared spectra were determined on compounds in potassium bromide discs with a Perkin–Elmer "Infracord."

3,5-Dimethoxybenzoyl chloride. 3,5-Dimethoxybenzoic acid (18·8 g.) was heated under reflux with thionyl chloride (16 g.) for 1½ hr.; the product had b. p. 118—120°/3 mm. (20 g., 92%).

Methyl 3,5-dimethoxyphenylacetate (Ib). A solution of the above acyl chloride (20 g.; 0·1 mole) in dry ether (50 ml.) was added, with stirring, to an ethereal solution of diazomethane

* Part IX, preceding paper.

[1] Astill and Roberts, *J.*, 1953, 3302.
[2] Davies, King, and Roberts, *J.*, 1955, 2782.
[3] Birch and Donovan, *Austral. J. Chem.*, 1955, **8**, 529.
[4] Newman and Beal, *J. Amer. Chem. Soc.*, 1950, **72**, 5163.
[5] Cf. Burton and Praill, *J.*, 1950, 1203.
[6] Cf. Bentley, Dawson, and Spring, *J.*, 1952, 1763.

(0·4 mole). The solution was kept at room temperature for *ca.* 3 hr. Removal of the solvent, and of the excess of diazomethane, left the diazo-ketone as a yellow crystalline solid. To a solution of this material in dry methanol (400 ml.) was added [4] a solution of dry silver benzoate (1·7 g.) in triethylamine (15 ml.), followed by more silver benzoate (1·2 g.) in triethylamine until the evolution of nitrogen ceased. The mixture was boiled (charcoal) and filtered. Methanol was removed and an ethereal solution of the residue was extracted with aqueous sodium hydrogen carbonate solution. Removal of the ether and distillation of the residue gave the ester as a pale-yellow oil (14 g., 72%), b. p. 155—160°/15 mm.

Methyl 2-acetyl-3,5-dimethoxyphenylacetate (II). To a solution of the foregoing ester (4·0 g.) in a mixture of acetic anhydride (4·5 g.) and acetic acid (9·0 g.) were added five drops of aqueous perchloric acid (60%). The mixture was shaken occasionally during 15 min. and water was then added to decompose excess of the anhydride. The product was collected in ether and the ethereal solution was washed repeatedly with aqueous sodium hydrogen carbonate solution and then dried ($MgSO_4$). Removal of the ether gave an oil (4·3 g.) which yielded crystals (3·7 g., 77%), m. p. 60—61°, from light petroleum (b. p. 40—60°). Sublimation at 55°/0·1 mm. gave the *ester-ketone* as prisms, m. p. 64° [Found: C, 61·7, 62·5; H, 5·8, 6·4; OMe, 36·0. $C_{10}H_7O_2(OMe)_3$ requires C, 61·9; H, 6·4; OMe, 37·0%].

2-Hydroxy-5,7-dimethoxy-1,4-naphthaquinone (IVa). A solution of the ester-ketone (1·5 g.) in ethanol (20 ml.) was added slowly to a refluxing solution of sodium ethoxide (from 0·24 g. of sodium) in ethanol (30 ml.). The solution was heated under reflux for a further 20 min. and was then cooled. A stream of air was drawn through the solution during 4 hr. Removal of the ethanol left a bright-red solid which was treated with N-sulphuric acid (100 ml.). The product was filtered off, washed, and dried. Crystallisation from benzene gave dark-yellow prisms (*ca.* 1·0 g., 70%) which on sublimation (150°/0·1 mm.) gave the *quinone* as fluffy, pale-yellow needles, m. p. 218—219° (decomp.) (Found: C, 61·3; H, 4·2. $C_{12}H_{10}O_5$ requires C, 61·5; H, 4·3%), $\lambda_{max.}$ 214, 261, 302, 376, and 417 mμ (log ε, 4·52, 4·25, 4·08, 3·58 and 3·30, respectively).

2,5,7-Trimethoxy-1,4-naphthaquinone. Methylation of the foregoing quinone (130 mg.) and purification of the product as previously described [2] gave 2,5,7-trimethoxy-1,4-naphthaquinone (35 mg.) as golden-yellow prisms with the required [2] m. p. and ultraviolet absorption spectrum.

Flaviolin (*2,5,7-trihydroxy-1,4-naphthaquinone*) (IVb). 2-Hydroxy-5,7-dimethoxy-1,4-naphthaquinone (0·5 g.) was stirred into a melt [7] of anhydrous aluminium chloride (8 g.) and sodium chloride (1·4 g.) at 170°. The mixture was kept at this temperature for 2 min., was cooled slightly, and was then poured into 5N-hydrochloric acid (100 ml.). The black product was collected in ether–chloroform. The organic layer was exhaustively extracted with an aqueous solution of sodium hydrogen carbonate. Acidification of the alkaline solution and extraction with ether gave an orange-brown oil. Chromatography [1] of this oil in butanol on a column of powdered cellulose (impregnated with a phosphate buffer of pH 8·0) gave a red solid which crystallised from warm dioxan–benzene to give flaviolin (6 mg.) as bright-red rhombs, m. p. 250° (decomp.) unaltered by admixture with natural flaviolin. The synthetic material gave the colour reactions (on variation of the pH of its aqueous solution) previously described [1] for natural flaviolin. Ultraviolet light absorption (on samples freed from dioxan [1])—synthetic: $\lambda_{max.}$ 215, 262, 308, 400, and 451 mμ (log ε 4·41, 4·12, 3·95, 3·31, and 3·38, respectively; natural: $\lambda_{max.}$ 215, 262, 308, 403, and 452 mμ (log ε 4·43, 4·12, 3·93, 3·30, and 3·35 respectively). The synthetic and the natural substance had similar infrared spectra with significant peaks at 3230, 1675, 1630, and 1590 $cm.^{-1}$.

We thank the Department of Scientific and Industrial Research for a maintenance grant (to B. W. B.).

THE UNIVERSITY, NOTTINGHAM. [*Received, November 23rd,* 1961.]

[7] Cf. Brunner and Singule, *Monatsh.*, 1948, **79**, 81

387. *Rate of Amide Formation via Carbamic Carboxylic Anhydrides.*

By KENNETH D. KOPPLE and RONALD A. THURSACK.

THE reaction of alkyl isocyanates with carboxylic acids to yield amides, *via* mixed carbamic carboxylic anhydrides, has been suggested as a possible path for the polymerization of amino-acid *N*-carboxy-anhydrides.[1,2] To determine whether this process proceeds at rates sufficient to account for the observed velocities of aprotic base-catalyzed polymerizations of *N*-carboxy-anhydrides, we have studied the reaction of ethyl isocyanate and ethyl α-isocyanatoisohexanoate with phenylacetic acid. In 1,2-dimethoxyethane these pairs react according to equations (1) and (2). Formation of symmetrical acid

$$Ph{\cdot}CH_2{\cdot}CO_2H + R{\cdot}NCO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ph{\cdot}CH_2{\cdot}CO_2{\cdot}CO{\cdot}NHR \quad \ldots\ldots\ldots (1)$$

$$\downarrow k_2$$

$$Ph{\cdot}CH_2{\cdot}CO{\cdot}NHR + CO_2 \quad \ldots\ldots\ldots (2)$$

anhydride plus disubstituted urea, as occurs with aryl isocyanates,[3] is negligible. The reactions were followed by infrared spectrophotometry; the reaction constants so determined are given in Table 1.

TABLE 1.

Reaction constants for phenylacetic acid–isocyanate systems.[a]

Isocyanate	k_1/k_{-1} (l.mole^{-1})	10^4k_1 (l.mole^{-1} sec.$^{-1}$)	10^4k_2 (sec.$^{-1}$)
Et·NCO	2·4	18	0·24 (2·8[b])
Bu^{i}CH(CO$_2$Et)NCO	1·0	—	0·36

[a] In 1,2-dimethoxyethane, 24°. Reactants 0·2—0·7M. [b] In 1,2-dimethoxyethane, 0·03M in triethylamine.

A direct comparison of the observed velocity of aprotic base-catalyzed polymerization of *N*-carboxy-anhydrides with that expected for a path involving mixed carbamic carboxylic anhydrides is not possible on the basis of the tabulated data alone; the concentration of the postulated isocyanato-acid[2] CHR·CO$_2$H·NCO or of the mixed anhydride linkage –O·CO·NH·CHR·CO$_2$·CO·NH·CHR·CO– is still unknown. However, the extremely optimistic assumption of 0·1M-concentration for the latter yields an expected velocity, even with base catalysis, of about 3×10^{-5} mole l.$^{-1}$ sec.$^{-1}$ for reaction (2).

At the equally unlikely concentration of 0·1M for the isocyanato-acid, the velocity of formation of the mixed anhydride would be about 2×10^{-5} mole l.$^{-1}$ sec.$^{-1}$. These velocities are to be compared with an observed propagation velocity near 2×10^{-3} mole l.$^{-1}$ sec.$^{-1}$ for methoxide initiation at 0·2M-*N*-carboxy-anhydride and 0·005M-initiator,[5] or about half that for tertiary amine-catalyzed polymerization under comparable conditions.[6] Since the necessary reactions thus proceed too slowly to account for the observed polymerization velocities, the participation of isocyanato-acids or mixed carbamic carboxylic anhydrides in the polymerization of *N*-carboxy-anhydrides can be ruled unlikely.

Experimental.—The reaction of the acid–isocyanate pairs was followed at 24° by observing the isocyanate infrared absorption at 1280 cm.$^{-1}$, for which calibration plots were made. The

[1] Bayer, *Angew. Chem.*, 1954, **59**, *A*, 265.
[2] Kopple, *J. Amer. Chem. Soc.*, 1957, **79**, 6442.
[3] Naegli and Tyabji, *Helv. Chim. Acta*, 1934, **17**, 1931.
[4] Idelson and Blout, *J. Amer. Chem. Soc.*, 1958, **80**, 2387, have also suggested this structure as an intermediate in polymerizations of *N*-carboxy-anhydrides.
[5] Reference 4 gives for γ-benzyl-L-glutamic *N*-carboxy-anhydride propagation constants in the range 4·3—6·3M l.mole^{-1} sec.$^{-1}$ at 34° in dioxan.
[6] Ballard and Bamford, *J.*, 1956, 381.

reacting mixtures were contained in 0·028 mm. calcium fluoride cells; a Perkin–Elmer model 21 spectrophotometer was used. To first approximation it could be assumed that the equilibrium of equation (1) was established rapidly, and at various reactant concentrations consistent values for k_1/k_{-1} were obtained, the disappearance of isocyanate at the maximum anhydride absorption (1775 cm.$^{-1}$) being used. At this time no amide absorption (1670 cm.$^{-1}$) was yet observable. For ethyl isocyanate, individual values of k_1 and k_{-1} were obtained by analysis of the first portion of the reaction, the rate law $d[\text{Anhydride}]/dt = k_1[\text{Isocyanate}][\text{Acid}] - k_{-1}[\text{Anhydride}]$ being assumed, *i.e.*, anhydride decomposition being neglected. Values for the concentrations involved were obtained from the known initial values and the extent of disappearance of isocyanate.

When initial reactant concentrations were kept below 0·3M, the anhydride concentration at equilibrium was sufficiently low to permit the assumption of the rate law, $d[\text{Amide}]/dt = -d[\text{Isocyanate}]/dt = (k_1k_2/k_{-1})[\text{Isocyanate}][\text{Acid}]$, which fits the data obtained after the establishment of equilibrium and gives values of k_2 in agreement with those obtained by the method described below.

For initial concentrations of reactant above 0·3M, it was necessary to obtain a value for the extinction coefficient of the anhydride (from the ratio of absorbance at 1775 cm.$^{-1}$ to isocyanate reacted, measured at times before amide absorption appeared) and then to determine a series of values for k_2 by use of the expression

$$k_2 = \Delta([\text{Isocyanate}]_0 - [\text{Isocyanate}] - [\text{Anhydride}])/[\text{Anhydride}]_{av.}\Delta t$$

The values of k_2 so determined showed no detectable trend over the first 80% of amide formation, but did exhibit considerable scatter (+25%) because of errors involved in the photometric measurements.

This work was supported by the U.S. Public Health Service, National Institutes of Health.

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO,
CHICAGO, ILLINOIS. [*Received, July 17th*, 1961.]

---

388. *The Oxidation of Lower Titanium Chlorides by Carbon Tetrachloride by a Route involving a Carbonium Ion.*

By C. EDEN and H. FEILCHENFELD.

WE report elsewhere [1] that carbon tetrachloride decomposes ethylaluminium dichloride and there suggest a carbonium ion mechanism for fission of the aluminium–carbon bond.

The chlorinating action of carbon tetrachloride is, however, not limited to metallo-organic compounds. Metals and salts in the lower valency states can also be oxidized according to the general scheme, $2M^{n+} + 2CCl_4 \longrightarrow 2M^{(n+1)+}Cl^- + C_2Cl_6$, where $n = 0$—3 but is less than the maximum valency.

This reaction, though highly exothermic, does not take place spontaneously. Sodium can be kept in carbon tetrachloride; the mixture explodes when subjected to mechanical shock.[2,3] The reaction appears in this case to follow a free-radical mechanism. Aluminium is slowly attacked by carbon tetrachloride.[4–7] A free-radical mechanism has been favoured though it has been pointed out that the oxidation product, $AlCl_3$, accelerates the reaction.[5,7]

In the present work the effect of carbon tetrachloride on titanium trichloride has been investigated. The trichloride was prepared by a modification of Ruff and Neumann's

[1] Eden and Feilchenfeld, *J. Phys. Chem.*, in the press.
[2] Staudinger, *Angew. Chem.*, 1922, **35**, 657.
[3] Lenze and Metz, *Chem.-Ztg.*, 1932, **56**, 921.
[4] Rhodes and Carty, *Ind. Eng. Chem.*, 1925, **17**, 909.
[5] Stern and Uhlig, *J. Electrochem. Soc.*, 1952, **99**, 381, 389.
[6] Minford, Brown, and Brown, *J. Electrochem. Soc.*, 1959, **106**, 185.
[7] Brown, Cook, Brown, and Minford, *J. Electrochem. Soc.*, 1959, **106**, 192

method.[8] A portion of this salt was transferred under a vacuum to a reaction vessel containing a glass-enclosed magnetic stirring-bar. The vessel itself was connected to a vacuum-system and was equipped with a rubber gasket. Carbon tetrachloride was injected through the rubber gasket and the suspension was stirred at 25—30°. No gas was evolved. At the end of a week the titanium trichloride was titrated with ferric chloride; it was found that none of it had been oxidized. Another portion of titanium trichloride was treated similarly with carbon tetrachloride which had previously been saturated with aluminium chloride (the solubility of aluminium trichloride in carbon tetrachloride is exceedingly small [9]). After 3 hours' contact about 2% of the titanium salt had been oxidized. Then titanium dichloride was prepared by disproportionation of the trichloride at 450° and evacuation; titration showed that after 3 hours' contact with carbon tetrachloride saturated with aluminium chloride about 3% of the dichloride had been oxidized.

Experiments with added n-butyl bromide were of particular interest. Titanium trichloride (3—4 mmoles) was transferred under a vacuum to the reaction vessel; aluminium trichloride (~5 mmoles) was sublimed into the vessel from a side-arm which was then sealed off; carbon tetrachloride (5 ml.) was injected and was followed by various amounts of n-butyl bromide. Irrespective of the amount of butyl bromide added, titration after 3 hours' contact showed 14%, and after 3 days' contact 50%, conversion of titanium trichloride into tetrachloride.

The following mechanism is proposed:

(1) $C_4H_9X + AlX_3 \rightleftharpoons C_4H_9^+AlX_4^-$ (X = Cl or Br)

(2) $C_4H_9^+AlX_4^- + TiCl_3 \rightleftharpoons C_4H_9\cdot + TiCl_3^+AlX_4^- \longrightarrow TiCl_3X + AlX_3$

(3) $C_4H_9\cdot + CCl_4 \longrightarrow C_4H_9Cl + CCl_3\cdot$

The butyl chloride formed in step (3) and the AlX_3 recovered in step (2) re-enter the reaction in step (1). The $CCl_3\cdot$ radicals recombine to give hexachloroethane (identified by gas chromatography). The oxidation step (2) shows how the overall reaction is catalyzed by carbonium ions; the alkyl free radical formed was scavenged by the solvent carbon tetrachloride; the overall reaction was simply $2TiCl_3 + 2CCl_4 \longrightarrow 2TiCl_4 + C_2Cl_6$.

The carbonium ion mechanism was supported by a side reaction. When the amount of n-butyl bromide added was between 0·05 and 0·10 ml., little liberation of butane was observed; with additions of 1 ml. of n-butyl bromide, up to 60% of the butyl was evolved as butanes (isobutane 57%, n-butane 43%). Since skeletal isomerization is promoted by a carbonium ion mechanism [10] this observation supports the proposed mechanism. The appearance of butanes in itself was not surprising. Friedel and Crafts [11] reported that a mixture of saturated hydrocarbons was formed by the action of aluminium chloride on isopentyl chloride. By extension of the mechanism [12] proposed for the exchange of halogen between alkyl halide and alkane in the presence of aluminium chloride one could write: $(C_4H_9)^+ + C_4H_9Cl = C_4H_{10} + (C_4H_8Cl)^+$

THE PETROCHEMISTRY LABORATORY OF THE NATIONAL COUNCIL FOR RESEARCH AND DEVELOPMENT AND OF THE DEPARTMENT OF PHYSICAL CHEMISTRY,
THE HEBREW UNIVERSITY,
JERUSALEM, ISRAEL.

[*Received, September 8th*, 1961.]

[8] Ruff and Neumann, *Z. anorg. Chem.*, 1923, **128**, 81.
[9] Wallace and Willard, *J. Amer. Chem. Soc.*, 1950, **72**, 5275.
[10] Condon, " Catalytic Isomerization of Hydrocarbons " in " Catalysis," Vol. VI, Reinhold, New York, 1958.
[11] Friedel and Crafts, *Ann. Chim.* (*France*), 1884, **1**, 451.
[12] Bartlett, Condon, and Schneider, *J. Amer. Chem. Soc.*, 1944, **66**, 1531.

389. *Oxidations of Organic Compounds with Quinquevalent Vanadium. Part XI.*[1] *Relative Rates of Alcohol Oxidation.*

By J. R. Jones and William A. Waters.

From the observation that the relative rates of oxidation of cyclohexanol and 1-deuterocyclohexanol by vanadium(v) in perchloric acid solution exhibited a primary isotope effect, $k_H/k_D = 3{\cdot}6$ at 50°, Littler and Waters[2] concluded that the rate-determining stage of the reaction led to the formation of the carbon radical $[CH_2]_5 > C(OH)\cdot$. If this is a general mechanism of oxidation of alcohols by vanadium(v), then allylic alcohols, $R{\cdot}CH{:}CH{\cdot}CH_2OH$, should yield mesomeric radicals, $CHR{:}CH{\cdot}CH(OH)\cdot \leftrightarrow \cdot CHR{\cdot}CH{:}CH{\cdot}OH$, and consequently should be oxidised much more easily than their saturated analogues. The tabulated results show that this is the case. As expected, the allylic alcohols are extensively degraded; after 1 week at 50° allyl alcohol had consumed 7·7 and crotyl alcohol 8·1 equiv. of vanadium(v).

Rates of oxidation of alcohols by vanadium(v) at 50°. Total ionic strength 3·1M; initial $[V^V] = 0{\cdot}05$M.

		In N-$HClO_4$		In 3N $HClO_4$	
Alcohol	Molarity	10^5k (sec.$^{-1}$)	10^5k/[Alcohol]	10^5k (sec.$^{-1}$)	10^5k/[Alcohol]
Pr^nOH	1·005	2·4	2·4	7·4	7·4
,,	2·01	4·5	2·3	14·4	7·2
Pr^iOH	1·00	0·75	0·75	2·3	2·3
Bu^nOH	0·404	0·92	2·3	3·7	9·1
Cyclohexanol	0·172	0·42	2·4	1·2	7·1
Allyl	0·127	—	—	29·7	237·0
,,	0·255	18·3, 18·3 *	72·0	63·5	249·0
Crotyl	0·252	18·5	73·0	51·7	205·0

* Under nitrogen.

Allyl and crotyl alcohol were dried and fractionated under nitrogen; the latter alcohol was made by reducing crotonaldehyde with sodium borohydride. The other alcohols were fractionated to constant b. p. Solutions were prepared in boiled-out, distilled water which was then saturated with nitrogen. The kinetic procedure was that of Part X.[1]

One of us (J. R. J.) thanks the D.S.I.R. for a research studentship.

The Dyson Perrins Laboratory, Oxford. [*Received, September 11th,* 1961.]

[1] Part X, *J.*, 1962, 1629.
[2] Littler and Waters, *J.*, 1959, 4046.

---

390. *The Addition of Phenyl Radicals to Sulphur Dioxide.*

By J. M. Squire and William A. Waters.

Although it is well known that olefins and sulphur dioxide can combine to form 1 : 1 copolymers in the presence of peroxide catalysts, little direct evidence of the nature and reactivity of the initial radical–sulphur dioxide adducts has been published.

When sulphur dioxide is passed into a decomposing, dry, solution of benzoyl peroxide in boiling benzene we have found that diphenyl disulphone, $Ph{\cdot}SO_2{\cdot}SO_2{\cdot}Ph$, is formed in about 4% yield together with the expected products of benzoyl peroxide decomposition in benzene solution; diphenyl sulphone, $Ph{\cdot}SO_2{\cdot}Ph$, could not be detected. In chlorobenzene at 100°, the yield of diphenyl disulphone rose to 14% but no chlorinated disulphone could be detected. This indicates that the sulphonyl radicals produced by reaction (2)

are too unreactive to attack benzene or chlorobenzene. However, when toluene was used the reaction product was benzyl phenyl sulphone, which we suggest is formed by the reactions (1)—(5) rather than by addition of benzyl radicals to sulphur dioxide, for in

$$(Ph{\cdot}CO_2{\cdot})_2 \rightleftharpoons 2Ph{\cdot}CO_2{\cdot} \longrightarrow Ph{\cdot} + CO_2 \quad (1)$$

$$Ph{\cdot} + SO_2 \longrightarrow Ph{\cdot}SO_2{\cdot} \quad (2)$$

$$2Ph{\cdot}SO_2{\cdot} \longrightarrow Ph{\cdot}SO_2{\cdot}SO_2{\cdot}Ph \quad (3)$$

$$Ph{\cdot}CO_2{\cdot} + CH_3{\cdot}Ph \longrightarrow Ph{\cdot}CO_2H + {\cdot}CH_2Ph \quad (4)$$

$$Ph{\cdot}SO_2{\cdot} + {\cdot}CH_2Ph \longrightarrow Ph{\cdot}SO_2{\cdot}CH_2{\cdot}Ph \quad (5)$$

this case dibenzyl sulphone and dibenzyl disulphone would be the expected products. Our results, which accord with those of Overberger and Rosenthal [1] on the decomposition of phenylphenylsulphonyldi-imide, show that phenyl radicals can combine with the sulphur atom of sulphur dioxide and then yield a stabilised free radical in which the unpaired electron is again associated with the sulphur atom. Some recent electron-spin resonance measurements support this view.[2]

Experimental.—A solution of benzoyl peroxide (25 g.) in dry benzene (250 ml.) was added dropwise during 4 hr. into a flask, heated under a reflux condenser, and through which a slow current of dry sulphur dioxide was passed. Refluxing and passage of sulphur dioxide was continued for a further 8 hr., the cooled liquid was washed with an excess of aqueous sodium carbonate, concentrated to 50 ml. under reduced pressure, and poured into light petroleum (300 ml.; b. p. 60—80°). A yellow powder (9·8 g.) containing sulphur was deposited; part (1·1 g.) of it was insoluble in benzene (50 ml.), and gave needles, m. p. 193—194° (from ethanol), undepressed on admixture with authentic diphenyl disulphone and having the characteristic sulphonyl absorption bands at 1325 and 1150 cm.$^{-1}$ and strong phenyl bands at 750 and 700 cm.$^{-1}$ (Found: C, 51·2; H, 3·3; S, 32·6. Calc. for $C_{12}H_{10}O_4S_2$: C, 51·1; H, 3·6; S, 22·7%). Biphenyl and unchanged benzoyl peroxide were isolated from the benzene and petroleum solution, but there was no evidence of the presence of diphenyl sulphone.

Sulphur dioxide was passed for 8 hr. through benzoyl peroxide (25 g.) in chlorobenzene (200 ml.) at 100°. On cooling, solid (1·3 g.) separated; more (2·7 g.) was obtained by neutralising the liquid, concentrating it, and pouring it into light petroleum. This again had m. p. and mixed m. p. 192—194° (Found: C, 51·0; H, 3·4; S, 22·5%). From a similar reaction in toluene the solid, precipitated with light petroleum and crystallised from benzene and ethanol, formed needles (3·7 g., 15%), m. p. 144·5—146°, unchanged on admixture with benzyl phenyl sulphone and having an identical infrared spectrum (Found: C, 67·0; H, 5·1; S, 14·0. Calc. for $C_{13}H_{12}O_2S$: C, 67·2; H, 5·2; S, 13·8%).

Reference compounds. Diphenyl disulphone (m. p. 193—194°) was made, as described by Hilditch,[3] by the permanganate oxidation of sodium benzenesulphinate in acetic acid, and benzyl phenyl sulphone (m. p. 146°) from benzyl chloride and sodium benzenesulphinate.[4]

THE DYSON PERRINS LABORATORY, OXFORD. [*Received, September 11th*, 1961.]

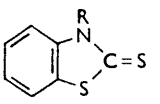
[1] Overberger and Rosenthal, *J. Amer. Chem. Soc.*, 1960, **82**, 117.
[2] Ayscough, Ivin, and O'Donnell, *Proc. Chem. Soc.*, 1961, 71.
[3] Hilditch, *J.*, 1908, **93**, 1526.
[4] Shriner, Struck, and Jorison, *J. Amer. Chem. Soc.*, 1930, **52**, 2060.

391. *The Structure of Mannich Bases Derived from 2-Thiobenzothiazoline.*

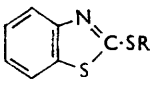
By K. N. Ayad, E. B. McCall, A. J. Neale, and L. M. Jackman.

Recent work,[1] concerned with the structure of the Mannich bases formed in the condensation of 2-thiobenzothiazoline * (I; R = H) with formaldehyde and amines (HNR'R''), has sought to distinguish between the isomeric forms (I and II; R = CH_2·NR'R'') by synthetical methods leading to the characterised 3-methyl-2-thiobenzothiazoline (I; R = Me).[2,4]

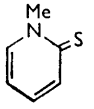
The differing ultraviolet absorption spectra of the isomers (I and II; R = Me) was considered by Sexton and Spinks [5] as evidence for the thione structure (I) of the hydroxymethyl and piperidinomethyl derivatives but might be regarded as inconclusive in view of recent work [1] and we have therefore investigated the nuclear magnetic resonance spectrum of the diethylaminomethyl derivative (R = CH_2·NEt_2).



(I)



(II)



(III)

We find the methyl groups of compounds (I and II; R = Me) to absorb at τ (p.p.m.) 6·19 and 7·32, respectively. The position of the former is in good agreement with the value (6·02) for the methyl group in 1-methyl-2-thiopyridine [6] (III) and indicates that the hetero-nitrogen atom has a very low charge density. By using these values for the methyl groups, in conjunction with Shoolery's effective shielding constant [7] for NR_2, values of 5·75 and 4·62 may be calculated for the methylene protons in (II and I, respectively; R = CH_2·NEt_2). Our value (4·82) is considered good evidence for the thione structure of this Mannich base.

There is a characteristic difference in the infrared spectra [8] of some isomers (I and II; R = Me, CH_2·NEt_2, CH_2Ph); we believe this difference, together with the ultraviolet absorptions, to be adequate to distinguish the isomeric forms, certainly where the substituent is an alkyl group or substituted alkyl group (R = $C_{16}H_{33}$, CH_2·CH_2·OH, CH_2·CH_2·NEt_2, or CH_2·CO_2Et) and probably when the substituent may interact conjugatively with the thiazoline ring (R = CO_2Et or Bz).

The Mannich base (I; R = CH_2·NEt_2) is formed by reaction of the sodium derivative of compound (I; R = H) with diethylaminomethyl chloride in ethanol or dry toluene. The high nucleophilic power of thio-anions [10] is presumably responsible for the high proportion of *S*-derivatives (II) formed in reaction with other halides (Cl·$C_{16}H_{33}$, Cl·CH_2·CH_2·NEt_2, Cl·CH_2·CH_2·OH, Cl·CO_2Et, Cl·CH_2·CO_2Et, Cl·COPh, Cl·CH_2Ph), and the preponderance of *N*-substitution by diethylaminomethyl chloride is probably connected with its predisposition to unimolecular substitution.

* Now proved [2,3] to have the thione structure under neutral conditions.

[1] Kolosova and Stavrovskaya, *Zhur. obshchei Khim.*, 1960, **30**, 689, 3576.
[2] Morton and Stubbs, *J.*, 1939, 1321; Koch, *J.*, 1949, 401.
[3] Oesper, Lewis, and Smyth, *J. Amer. Chem. Soc.*, 1942, **64**, 1130; Gur'yanova and Vasil'eva, *Zhur. fiz. Khim.*, 1954, **28**, 1319; Tashpulatov, Zvonkova, and Shdanov, *Kristallografiya*, 1957, **2**, 3847.
[4] Mills, Clark, and Aeschlimann, *J.*, 1923, **123**, 2362; Wheatley, *J.*, 1961, 4379.
[5] Sexton and Spinks, *J.*, 1948, 1717.
[6] Elvidge and Jackman, unpublished work.
[7] Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, p. 59.
[8] Lloyd and Neale, unpublished work.
[9] Reed, Robertson, and Sexton, *J.*, 1939, 473.
[10] de la Mare and Vernon, *J.*, 1956, 41.

Experimental.—Spectra. Nuclear magnetic resonance spectra were determined for 5% solutions in deuterochloroform with a Varian 4300 spectrometer operating at 56·445 Mc./sec. and 21°. The spectra were calibrated by the side-band technique and tetramethylsilane was employed as internal reference. Ultraviolet spectra (solutions in ethanol) were obtained by using a Unicam SP 700 spectrometer, and infrared spectra (solutions in carbon tetrachloride and carbon disulphide) by using a Grubb–Parsons S4 or a Unicam SP 100/130 spectrometer.

Materials. The sodium derivative of 2-thiobenzothiazoline was prepared in aqueous solution at 50°, a slight excess of thione being used. Filtration and drying at 23 mm. and then 40° gave the derivative which was used without further treatment except where stated.

3-*Diethylaminomethyl-2-thiobenzothiazoline* (I; R = CH_2·NEt_2). (i) The conditions were essentially those of Robinson *et al.*[11] The product (yield 63·5%), crystallised from light petroleum (b. p. 60—80°), had m. p. 83—85° (Found: C, 57·3; H, 7·0; N, 10·9; S, 24·9. Calc. for $C_{12}H_{16}N_2S_2$: C, 57·1; H, 6·4; N, 11·1; S, 25·4%), $\lambda_{max.}$ 230, 248, 326 mμ (ε 13,800, 14,500, 27,200, respectively).

(ii) (*a*) To a stirred suspension of the sodium derivative (dried at 180°/1·5 mm.; 0·087 mole) in azeotropically dried toluene (150 ml.) at 40° was added diethylaminomethyl chloride[12] (0·087 mole) covered with the same solvent (75 ml.). After reaction at room temperature for 5 hr. and at 45° for 0·5 hr., the mixture was filtered and the filtrate washed with water and dried ($MgSO_4$). Removal of solvent and extraction of the residue with hot light petroleum (b. p. 60—80°) gave a product (13·3 g., 60·0%) identical with the previous one in m. p., mixed m. p., and ultraviolet and infrared spectra.

(*b*) Reaction of the sodium derivative (0·12 mole) in ethanol (75 ml.) with diethylaminomethyl chloride (0·12 mole) in ethanol (25 ml.) under reflux for 3 hr., and working up as in (*a*) gave the same product (17·8 g., 60·8%).

2-2′-*Diethylaminomethylthiobenzothiazole* (II; R = CH_2·CH_2·NEt_2). 2-Diethylaminoethyl chloride (0·11 mole) reacted with the above sodium derivative (0·11 mole) in refluxing ethanol for 2·5 hr. After filtration and removal of solvent, the product was removed in ether, washed with 2N-sodium hydroxide and water, dried ($MgSO_4$), recovered (20·0 g., 67·5%), and distilled; it had b. p. 159°/0·85 mm., n_D^{25} 1·6122 (Found: C, 58·6; H, 6·7; N, 10·6; S, 24·0. $C_{13}H_{18}N_2S_2$ requires C, 58·7; H, 6·8; N, 10·5; S, 24·1%), $\lambda_{max.}$ 280, 288, 300 mμ (ε 12,600, 11,860, 9730, respectively).

2-2′-*Hydroxyethylthiobenzothiazole* (II; R = CH_2·CH_2·OH). Prepared essentially according to the method of Reed *et al.*[9] (3·7 moles of ethylene chlorohydrin and 1 mole of the sodium derivative) in 83% yield, this compound had m. p. 53—55°, $\lambda_{max.}$ 282, 290, 300 mμ (ε 11,800, 10,600, 8680, respectively).

2-*Ethoxycarbonylthiobenzothiazole* (II; R = CO_2Et). Heating the sodium derivative (0·20 mole) and ethyl chloroformate (0·20 mole) in alcohol and extracting the crude product with hot light petroleum (b. p. 60—80°) gave 2-*ethoxycarbonylthiobenzothiazole* (56·5%), m. p. 62—64° (Found: C, 50·4; H, 3·8; N, 5·8; S, 26·7. $C_{10}H_9NO_2S_2$ requires C, 50·2; H, 3·8; N, 5·8; S, 26·8%), $\lambda_{max.}$ 273 mμ [ε 14,500 (fine structure not resolved)]. The residue from the extraction proved to be the thione (I; R = H) of 92·5% purity.

2-*Ethoxycarbonylmethylthiobenzothiazole* (II; R = CH_2·CO_2Et). (*a*) The sodium derivative (0·10 mole) and ethyl bromoacetate (0·10 mole) in dry toluene, as above, gave this product (82·2%), m. p. 41—42° [from light petroleum (b. p. 60—80°)], $\lambda_{max.}$ 276, 288, 298 mμ (ε 12,600, 11,400, 8300). Kucherov[13] gives m. p. 42—44°.

(*b*) The sodium derivative (0·15 mole) and ethyl chloroacetate (0·15 mole) in refluxing ethanol gave the same product (70·8%), b. p. 148—150°/0·4 mm., m. p. 41—42°.

2-*Benzoylthiobenzothiazole* (II; R = COPh). The sodium derivative (0·10 mole) and benzoyl chloride (0·10 mole) in acetone gave this product (88·5%), m. p. 126—127° (from benzene–light petroleum) (Found: C, 61·9; H, 3·1; N, 5·5; S, 23·5. Calc. for $C_{14}H_9NOS_2$: C, 61·9; H, 3·3; N, 5·2; S, 23·6%), $\lambda_{max.}$ 278, 312 mμ (ε 12,800, 12,00). Kiyaki and Yamagishi[14] give m. p. 129—131°.

2-*Benzylthiobenzothiazole* (II; R = CH_2Ph). Prepared in alcohol (yield 68·3%), this

[11] Robinson, Bunbury, Davies, and Naunton, B.P. 377,253/1932.
[12] Bohme and Ellenberg, *Chem. Ber.*, 1959, **92**, 2976.
[13] Kucherov, *Zhur. obshchei Khim.*, 1949, **19**, 752.
[14] Kiyaki and Yamagishi, *J. Pharm. Soc. Japan*, 1956, **76**, 1196.

derivative had m. p. 40—41° (from benzene), $\lambda_{max.}$ 283, 290, 300 mμ (ε 13,150, 12,600, 10,650). Moore and Waight [15] give m. p. 39·5—40·5°, $\lambda_{max.}$ very similar.

2-Cetylthiobenzothiazole (II; R = $C_{16}H_{33}$). This derivative, obtained similarly (from equimolar amounts of reactants) in 99% yield, had m. p. 43—44° (from ethanol) (Found: C, 70·6; H, 9·5; N, 3·4; S, 16·4. $C_{23}H_{37}NS_2$ requires C, 70·6; H, 9·6; N, 3·5; S, 16·2%), $\lambda_{max.}$ 282, 290, 302 mμ (ε 11,600, 10,500, 8600).

MONSANTO CHEMICALS LIMITED, RUABON, DENBIGHSHIRE (K. N. A., E. B. M., A. J. N.).
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
S. KENSINGTON, LONDON, S.W.7 (L. M. J.). [*Received, September 13th*, 1961.]

[15] Moore and Waight, *J.*, 1952, 4237.

---

392. *The Interaction of Silicon Tetrachloride and Water in the Gaseous Phase.*

By I. R. BEATTIE and G. MCQUILLAN.

HUDSON [1] has stated that there is no reaction when silicon tetrachloride is mixed with water in the gaseous phase at temperatures in the range 25—100°. No experimental results were given to support this claim which, from the diagram of the apparatus used, appears to be based solely on pressure measurements. The reaction

$$SiCl_4(g) + 2H_2O(g) \longrightarrow SiO_2(s) + 4HCl(g)$$

involving a pressure increase in a constant volume system is thermodynamically favourable. Any lack of reactivity must thus be attributed to kinetic effects. The inertness of carbon tetrahalides to hydrolysis is usually attributed [2] to " their being covalently saturated," unlike the tetrahalides of silicon, which readily function as weak Lewis acids. Although it is probable that most co-ordination compounds of silicon tetrachloride are effectively fully dissociated in the gas phase, it would be surprising if kinetically significant amounts of " complex " were not present.

Treatment of silanols under appropriate conditions with hydrogen halide yields silyl halides, which are readily hydrolysed back to the silanols.[3] Correspondingly, silylamines readily form halogeno-compounds on treatment with hydrogen halide. This reaction occurs so readily that Bailey *et al.*[4] have used it preparatively and Gilman and Dunn [5] have suggested that no amine salts of silylamines exist, owing to the ease of formation of the Si–X bond. The monohydrochloride of trichlorodimethylaminosilane is, however, known.[6] Ammonolysis of chlorosilanes occurs readily and apparently silicon tetrachloride reacts with ammonia in the gaseous phase.[7] It is evident that in reactions of this kind series of equilibria are possible. This is confirmed by some work on the hydrolysis of trialkylchlorosilanes, where equilibria of the type $2R_3SiCl + H_2O \rightleftharpoons (R_3Si)_2O + 2HCl$ have been reported, with no silanol present at equilibrium.[8] It is thus reasonable to suppose that in the gas-phase hydrolysis of silicon tetrachloride equilibria of the type

$$SiCl_4 + H_2O \rightleftharpoons SiCl_3{\cdot}OH + HCl \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$2SiCl_4 + H_2O \rightleftharpoons Si_2OCl_6 + 2HCl \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

[1] Hudson, Proc. Internat. Congr. Pure Appl. Chem., London, 1949, **11**, 297.
[2] Sidgwick, " The Chemical Elements and Their Compounds," Oxford, 1950.
[3] Sommer, Pieztrusza, and Whitmore, *J. Amer. Chem. Soc.*, 1946, **68**, 2282.
[4] Bailey, Sommer, and Whitmore, *J. Amer. Chem. Soc.*, 1948, **70**, 435.
[5] Gilman and Dunn, *Chem. Rev.*, 1953, **52**, 77.
[6] Cass and Coates, *J.*, 1952, 2347.
[7] Billy, *Compt. rend.*, 1956, **242**, 137.
[8] Hyde, Brown, and Smith, *J. Amer. Chem. Soc.*, 1960, **82**, 5854.

will be significant. The compound $SiCl_3$·OH has been isolated by two groups of workers.[9,10] Although there are discrepancies between the properties recorded it appears that trichlorosilanol is a fairly volatile liquid (b. p. about 110°) which in condensed phases readily polymerises with loss of hydrogen chloride. Similarly, hexachlorodisiloxane has been isolated [11] as a liquid with b. p. of 137° and with a vapour pressure of about 1·5 cm. at 50°.

It is interesting to compare equations (1) and (2) with the analogous equation for ammonolysis:

$$SiCl_4 + NH_3 \longrightarrow SiCl_3{\cdot}NH_2 + HCl \quad . . . . . (3)$$

$$2SiCl_4 + NH_3 \longrightarrow Si_2NHCl_6 + 2HCl \quad . . . . . (4)$$

Although hexachlorodisilazane [12] has been prepared by high-temperature ammonolysis of silicon tetrachloride, it is to be expected that at a lower temperature, where ammonium chloride would be precipitated from the gaseous phase, the reaction would become heterogeneous, leading to $Si(:NH)_2$.

We carried out some initial experiments to confirm Hudson's results. Runs 1 and 2 of the Table demonstrate that under conditions of rigorous cleanliness silicon tetrachloride and water, when mixed in the gas phase at 50°, yield the same pressure as is calculated from the gas laws. Observations showing " no reaction " were obtained only in clean bulbs which had not been used previously for the reaction. Attempts to repeat experiments, in bulbs which had been previously used *and* shown no apparent reaction, led to variable results; frequently the pressure readings increased slowly with time, indicating a heterogeneous reaction with the production of silica. These findings agree with Hudson's;

Pressure–volume relations in the system $SiCl_4$–NMe_3–H_2O.

		Pressure, in cm. (volume, in c.c.)				
Run	Temp.	$SiCl_4$	H_2O	NMe_3	Mixture	Calc.
1	50·7°	3·185 (139)	1·239 (310)	—	2·66 (311)	2·660 *
2	50·2	1·915 (139)	1·005 (310)	—	1·856 (311)	1·858 *
3	26·1	4·210 (139)	—	7·109 (324)	6·171 (463)	6·230 *
4	50·0	0·543 (339)	0·818 (339)	0·447 (339)	1·300 (339)	1·325 †
						1·808 *

* On the assumption that there is no reaction.

† For $SiCl_4(g) + 4NMe_3(g) + 2H_2O(g) \longrightarrow SiO_2(s) + 4NMe_3HCl(s)$ and $SiCl_4(g) + 2H_2O(g) \longrightarrow 4HCl(g) + SiO_2(s)$.

he found that in bulbs containing silica the pressure increased over a period of about twenty minutes. We then studied the reaction of silicon tetrachloride with water in the presence of trimethylamine as a Lewis base to act as a hydrogen chloride acceptor. In view of the known instability of the 1 : 1 addition compound of silicon tetrachloride with trimethylamine, virtual absence of reaction in the vapour phase was expected. This is confirmed by run 3 of the Table. However, when a mixture of trimethylamine and water was allowed to react with silicon tetrachloride in the gaseous phase, there was rapid reaction with the production of a fluffy deposit (trimethylammonium chloride and silica), presumably from the gas phase.

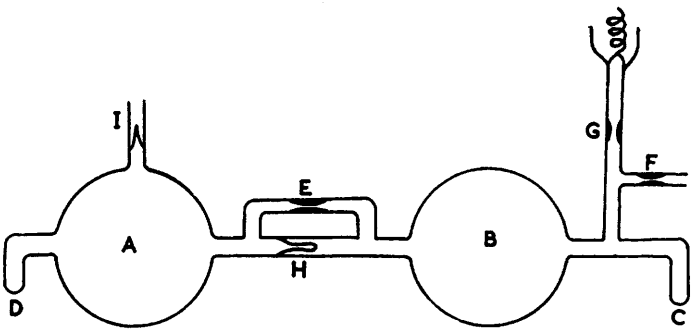
Run 4 gives an example of the pressure readings obtained. The interpretation of such results is difficult in view of the introduction of a large surface area into the reaction cell on which subsequent heterogeneous reactions could occur. A further possibility is catalysis of the heterogeneous reaction owing to the presence of hydrogen chloride in the silicon tetrachloride. However, in view of the extreme care taken in the preparation of the silicon tetrachloride we consider that these results support the postulate that a mixture

[9] Emeleus and Welch, *J.*, 1939, 1928.
[10] Goubeau and Warncke, *Z. anorg. Chem.*, 1949, **259**, 109.
[11] Schumb and Stevens, *J. Amer. Chem. Soc.*, 1947, **69**, 726.
[12] Schumb and Towle, *J. Amer. Chem. Soc.*, 1953, **75**, 6085.

of silicon tetrachloride and water in the gaseous state is in equilibrium with hydrogen chloride and some unknown species.

A more elegant method of examination would show the presence of hydrogen chloride in such a mixture. Hydrogen chloride has rather intense infrared bands around 3000 cm.$^{-1}$, where it is feasible to use fused silica windows. Thus silicon tetrachloride and water were mixed in the gaseous phase under a variety of experimental conditions and the infrared spectra observed, occasionally with simultaneous pressure measurement. In no case was mixing attained without the rapid production of considerable quantities of hydrogen chloride. In all our experiments an excess of silicon tetrachloride was used in terms of reaction (2), presumably favouring the production of compounds such as hexachlorodisiloxane rather than those with free hydroxyl linkages.

At temperatures in the region of 25° we frequently found that mixing silicon tetrachloride and water in the gaseous phase caused a slight increase in pressure, much less than was required for reaction to yield silica and hydrogen chloride. Further, when these mixtures were kept for several days there was no visible silica in the cell. However, the gaseous products were almost exclusively hydrogen chloride. The glass vessel in which the reaction had been carried out appeared to be perfectly clean, apart from a slight iridescence on the surface.



The apparatus.

Experimental.—Silicon tetrachloride was fractionally distilled and then distilled several times *in vacuo*. Residual traces of hydrogen chloride were removed with pyridine, followed by distillation *in vacuo*. Trimethylamine was purified by treatment with silicon tetrachloride, addition of pyridine, and distillation *in vacuo*. Distilled water was distilled twice *in vacuo*.

Techniques. The reagents were dispensed from storage tubes by means of diaphragm taps. Mixing was accomplished by using diaphragm taps (with and without a mercury reservoir to force one gas into a bulb containing the other), or specially designed break-seals. These seals were such that, on breaking, only one clean cut appeared (to reduce the possibility of heterogeneous reaction on the freshly fractured surface). Pressures were measured by means of mercury manometers, with and without a spiral gauge as a null-point instrument. Silica windows were joined to the 10 cm. infrared cells either by a thin film of inert adhesive or by direct fusion.

The Figure illustrates the experimental technique used in one of the later experiments. The apparatus shown was wholly contained in a large thermostat bath and the infrared cell, with necessary appendages, could be removed in its own smaller thermostat bath for the appropriate spectral measurements. Silicon tetrachloride was introduced into bulb A and cell B by means of the cold finger C. The pressure was measured and the whole of the silicon tetrachloride transferred to bulb A by use of the cold finger D; then constriction E was sealed. Water was then introduced into B and condensed in the cold finger C; then the apparatus was sealed off at F. The pressure of the water vapour was measured at the thermostat temperature, the water recondensed in C, and the apparatus sealed off at G. The inner thermostat bath could then be removed and the infrared cell (fitted with double windows to avoid heat loss)

placed in the sample beam of a Perkin–Elmer 221 infrared spectrometer. The silicon tetrachloride pressure and bulb volume were selected relative to the infrared cell volume and water pressure, so that the silicon tetrachloride was forced into the infrared cell by virtue of its higher pressure, with little transfer in the opposite direction. The water pressure was also selected so that direct compression by the rush of silicon tetrachloride vapour, before adequate mixing had occurred, could not cause condensation. The hydrogen chloride bands were observed as a function of time after breaking of septum H. Finally, the cell could be reconnected to the spiral gauge, breaker I broken, and the resultant pressure measured. After calibration of the relevant volumes the pressure changes could be assessed.

Deposit in the reaction of silicon tetrachloride with water in the presence of trimethylamine. The infrared spectrum (2—15 μ) of the deposit, taken as a Nujol mull with dry-box techniques, agreed with that to be expected for a mixture of trimethylammonium chloride and silica. The trimethylammonium chloride was sublimed from the silica *in vacuo* and the products were re-examined by infrared spectroscopy.

The authors thank the Department of Scientific and Industrial Research for a grant (to G. M.) and for purchase of the spectrometer.

KING'S COLLEGE UNIVERSITY OF LONDON,
STRAND, W.C.2.

[*Received, September 14th*, 1961.]

393. *Esterification of Bis-2-hydroxyethylamine.*

By E. N. GABALI and Y. M. ABOU-ZEID.

ESTERIFICATION of bis-2-hydroxyethylamine with acetic acid, acetic anhydride,[1] and keten [2] yields the corresponding diester and the diester-amide while with benzoyl chloride and *p*-nitrobenzoyl chloride only the diester-amide is obtained.[3]

We have found that when one molecule of diethanolamine is treated with two molecules of benzoyl chloride the diester alone is obtained, but with *p*-nitrobenzoyl chloride the same conditions give the diester-amide.

Nevertheless the corresponding mono- and di-*p*-nitrobenzoates were separately prepared, the former through protonation of the amino-group of the ethanolamine and reaction with the acid chloride, and the latter by reaction of bis-2-chloroethylamine and silver *p*-nitrobenzoate.

Experimental.—Bis-2-benzoyloxyethylamine hydrochloride. Schotten–Baumann esterification of diethanolamine (1 mole) with redistilled benzoyl chloride (2 moles) gave an oil. Its ethereal extract gave, on passage of dry hydrogen chloride, a *salt* which crystallised from alcohol–ether as yellow clusters, m. p. 138—140° (Found: C, 61·2; H, 5·7; Cl, 9·3; N, 4·0. $C_{18}H_{20}ClNO_4$ requires C, 61·8; H, 5·7; Cl, 10·15; N, 4·0%).

The diester-amide, from *p*-nitrobenzoyl chloride (2 moles), was obtained as pale yellow needles, m. p. 156—157° (from acetone) (lit.,[3] m. p. 149—150°) (Found: C, 54·4; H, 3·6; N, 10·1. Calc. for $C_{25}H_{20}N_4O_{11}$: C, 54·3; H, 3·65; N, 10·1%).

N-2-*Hydroxyethyl*-N-2-p-*nitrobenzoyloxyamine hydrochloride.* Diethanolamine (2 g.) in chloroform (30 c.c.) was saturated with dry hydrogen chloride, *p*-nitrobenzoyl chloride (6·5 g.) in chloroform (60 c.c.) was then added, and the mixture heated at 45—55° for 120 hr. After removal of chloroform the residue crystallised from ethanol–ether as pale yellow granules, m. p. 168—170° (Found: C, 45·7; H, 5·25; Cl, 12·05; N, 9·8. $C_{11}H_{15}ClN_2O_5$ requires C, 45·45; H, 5·25; Cl, 12·2; N, 9·65%).

Di-(2-p-*nitrobenzoylethyl*)*amine.*—Bis-2-chloroethylamine (2 g.) (liberated from the hydrochloride [3] by use of dry carbon dioxide-free air, to avoid dimerisation of the base) and silver

[1] Mann, *J.*, 1934, 461.
[2] Ponomarev and Isaev, *Zhur. obshchei Khim.*, 1952, **22**, 652.
[3] Brintzinger and Koddebush, *Chem. Ber.*, 1949, **82**, 201.

p-nitrobenzoate (7·7 g., 2 equiv.) were heated at 130—140° for 10 min., and then cooled in an ice-bath. Sodium-dried benzene (100 c.c.) was added, the mixture kept at room temperature for 24 hr., and refluxed for 48 hr., and silver chloride filtered off while hot. On cooling, the filtrate yielded the *diester* (4·5 g.) as pale yellow crystals, m. p. 165—167° (Found: C, 53·3; H, 4·35; N, 9·9. $C_{18}H_{17}N_3O_8$ requires C, 53·6; H, 4·2; N, 10·4%). The yield depended on the time of initial heating.

ORGANIC CHEMISTRY DEPARTMENT, FACULTY OF PHARMACY,
CAIRO UNIVERSITY. [*Received, September 22nd*, 1961.]

---

394. *Preparation and Purification of Diborane.*

By C. J. DANBY, E. GOBBETT, and J. W. LINNETT.

FOR some work on the oxidation of diborane, it was necessary to obtain the hydride free from impurities which might affect the oxidation process. Preliminary work [1] had shown that hydrocarbons and their derivatives exerted a marked inhibiting effect and therefore such compounds had to be eliminated.

Diborane was prepared by the reduction of boron trifluoride with lithium aluminium hydride; [2] in later experiments lithium borohydride was used as the reducing agent. The boron trifluoride was used as the etherate, which was redistilled on the day of use. The reaction was carried out in ether, which was dried successively by calcium chloride, sodium, and lithium hydride.

Boron trifluoride was added to a slurry of the lithium aluminium hydride in ether in a flask through which nitrogen passed continuously. The nitrogen left the flask *via* a reflux condenser cooled in acetone and solid carbon dioxide, then through a trap similarly cooled and finally through two traps cooled in liquid air (all traps were protected by metal sheaths). Any permanent gas trapped in the solid was removed by repeated vaporisation, condensation, and evacuation. The diborane was finally vaporised into a storage vessel. In this preparation the boron trifluoride was in excess and yields of 40 to 70% were obtained. The quantity of diborane produced in a single preparation was always less than 1 g.

Mass-spectrometric analysis showed that the diborane was free from ether but contained an impurity characterised by a prominent peak at *m/e* 47. The concentration of this impurity varied from preparation to preparation. A sample was isolated by gas chromatography and identified as ethyl fluoride by mass-spectrometer (the prominent ion at *m/e* 47 being $C_2H_4F^+$). This suggests that " active fluorine " (perhaps atomic) may be formed as an intermediate and attacks the ether to some extent, though ethyl radicals would also be likely to produce ethyl fluoride. The amount of ethyl fluoride tended to be smaller when the starting material was borohydride.

Ethyl fluoride is less volatile than diborane (at −92°c the vapour pressures are 20 and 760 mm., respectively). We considered therefore the possibility of using a less volatile ether (*e.g.*, propyl) but concluded that obtaining the starting materials would be more difficult and the course of the reaction might be affected. We therefore constructed a Rose fractionating column [3] modified to operate below atmospheric pressure. The small thimble-shaped still was electrically heated and was joined to an air-jacketed column about 30 cm. long. The condenser at the top of this column was made of brass and packed with lead shot to increase its thermal capacity. The still, column, and condenser were contained in a long Dewar vessel. The condenser was cooled with liquid air (supplied at a steady rate from another Dewar vessel), and the cold air issuing from the condenser was

[1] Gobbett and Linnett, unpublished work.
[2] Shapiro, Weiss, Schmich, Skolnik, and Smith, *J. Amer. Chem. Soc.*, 1952, **74**, 901.
[3] Rose, *Ind. Eng. Chem.*, 1940, **32**, 668.

carried by a tube to the bottom of the long Dewar vessel to keep the column cool. Four thermocouples were located in the still, in the middle and outside of the column-jacket, and in the take-off side arm. The diborane was withdrawn into a storage vessel through a needle valve: this valve and the still-heating current were adjusted to keep the conditions of temperature and pressures steady (the pressures in the column and beyond the needle valve were measured on two manometers). Distillations were carried out in the neighbourhood of 140°K at which the vapour pressure of diborane is between 50 and 100 mm. and that of ethyl fluoride less than 1 mm. The vapour coming off before the conditions became steady was discarded and when the temperature recorded by the still and side-arm thermocouples began to rise the needle valve was closed.[4] Mass spectrometric analysis was unable to detect any ethyl fluoride in this fractionated diborane.

This work was supported by a grant from the Department of Scientific and Industrial Research.

PHYSICAL AND INORGANIC CHEMISTRY LABORATORIES,
OXFORD. [*Received, October 24th*, 1961.]

[4] For further details, see E. Gobbett, D.Phil. Thesis, Oxford, 1961.

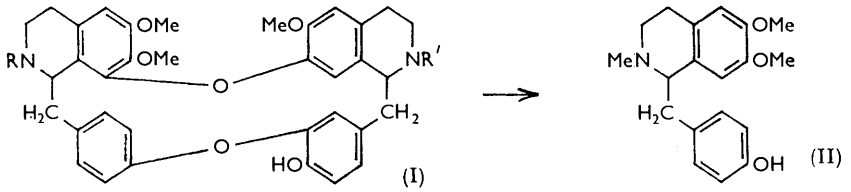
---

395. *Alkaloids from Greenheart. Part II.*[1] *Sepeerine.*

By M. F. GRUNDON and J. E. B. MCGARVEY.

SEPEERINE was shown previously [1] to be a de-*N*-methyloxyacanthine, but it was not possible to distinguish between the two structures (I; R = H, R′ = Me) and (I; R = Me, R′ = H), differing in the position of a secondary amino-group. The complete structure of the alkaloid has now been determined.

N-Acetylsepeerine [1] with diazomethane gave an amorphous compound, which was apparently *N*-acetyl-*O*-methylsepeerine as it had an infrared maximum at 1642 cm.$^{-1}$ (⟩NAc) and did not absorb in the 3000—3500 cm.$^{-1}$ region. Reductive cleavage of the methylation product with sodium in liquid ammonia gave two phenolic fractions, one of which was basic and one non-basic. The basic fraction, purified through its crystalline oxalate, was shown to be (+)-armepavine (II).



Thus, sepeerine has the structure (I; R = Me, R′ = H). This conclusion was confirmed by showing by direct comparisons that *O*-methylsepeerine dihydrochloride [1] was identical with *OO*-dimethyltrilobamine dihydrochloride,[2] and that sepeerine differed from the other de-*N*-methyloxyacanthine (I; R = H, R′ = Me) (dihydrohypoepistephanine-A), which has been described recently.[3]

Experimental.—Reductive fission of the methylation product of N*-acetylsepeerine.* Ethereal diazomethane (from 7 g. of methylnitrosourea) was added to a solution of *N*-acetylsepeerine [1]

[1] Part I, Grundon and McGarvey, *J.*, 1960, 2739.
[2] Inubushi, *Pharm. Bull.* (*Japan*), 1955, **3**, 384.
[3] Watanabe, *Yakugaku Zasshi*, 1960, **80**, 166.

(1·11 g.) in methanol (50 c.c.). After 5 days the solution was filtered and evaporated to give the methylation product.

The methylation product (1·10 g.) in toluene (60 c.c.) was added slowly to a solution from sodium in liquid ammonia (800 c.c.). Sodium (total 1·25 g.) was added in portions until the mixture remained blue for 15 min. After evaporation of the ammonia, the toluene solution was shaken with several portions of N-sodium hydroxide and evaporated, giving a gum (0·11 g.), which was probably unchanged *N*-acetyl-*O*-methylsepeerine.

The alkaline solution was acidified with N-hydrochloric acid and extracted with chloroform, giving the non-basic product as a brown solid (0·22 g.) which was not obtained crystalline. The acid solution was made alkaline with sodium hydrogen carbonate and extracted with chloroform. Evaporation of the chloroform gave the basic product (0·27 g.), which was converted with oxalic acid in ethanol into (+)-armepavine oxalate (0·19 g.), separating from ethanol in needles (0·17 g.), m. p. 211—213°; the infrared spectrum was identical with that of (−)-armepavine oxalate, m. p. 211—212°.

The oxalate was converted into (+)-armepavine, crystallising from light petroleum (b. p. 40—60°) in needles (0·11 g.), m. p. 145—146°, $[\alpha]_D^{17}$ +102° (*c* 0·52 in $CHCl_3$); the infrared spectrum was identical with that of (−)-armepavine, m. p. 145—146° {lit.,[4] $[\alpha]_D^{21}$ −105° (*c* 1·25 in $CHCl_3$)}.

O-*Methylsepeerine dihydrochloride and sepeerine.* *O*-Methylsepeerine dihydrochloride, decomp. 230—235°, $[\alpha]_D^{17}$ +235° (*c* 0·2 in H_2O), was identical (infrared) with *OO*-dimethyltrilobamine dihydrochloride, decomp. 232—237° {lit.,[2] $[\alpha]_D^{20}$ +272° (*c* 0·47 in H_2O)}.

The infrared spectrum of sepeerine, m. p. 197—199°, $[\alpha]_D^{20}$ +391° (*c* 0·3 in $CHCl_3$), differed from that of dihydrohypoepistephanine-A, m. p. 217—218° (lit.,[3] $[\alpha]_D^{20}$ +263°).

We thank Dr. Y. Inubushi, Professor M. Tomita, and Dr. J. Walker for alkaloid samples, the Tropical Products Institute for a supply of greenheart bark, and the Ministry of Education for Northern Ireland for a postgraduate studentship (to J. E. B. McG.).

THE QUEEN'S UNIVERSITY, BELFAST. [*Received, November 15th*, 1961.]

[4] Kidd and Walker, *J.*, 1954, 669.

---

396. *The Bromides and Oxide Bromides of Rhenium.*

By R. COLTON.

HAGAN and SIEVERTS [1] found in 1933 that passing bromine vapour over heated rhenium gave a green material which they described as the tribromide and said sublimed easily in a vacuum. They also noted that when oxygen was present a blue solid was obtained to which they assigned formula ReO_2Br_2. There appears to have been no further work on this reaction. A tetrabromide has been prepared by reducing perrhenic acid with hydrobromic acid.[2] Perrhenyl bromide, ReO_3Br, is the only other known oxide bromide.[2,3] This suggested that the rhenium–bromine system differed considerably from that of rhenium–chlorine. Chlorine and the metal give almost exclusively the pentachloride which when heated in a stream of nitrogen leaves rhenium trichloride. Rhenium tetrachloride is unknown and perrhenyl chloride, ReO_3Cl, and rhenium oxide tetrachloride, $ReOCl_4$, are the only known oxide chlorides.[4] However, we find a close similarity between the two systems, as shown in the Table.

Re^{VII}	Re^{VI}	Re^{V}	Re^{IV}	Re^{III}
ReO_3Cl	$ReOCl_4$	$ReCl_5$	—	$ReCl_3$
ReO_3Br	$ReOBr_4$	$ReBr_5$	$ReBr_4$	$ReBr_3$

[1] Hagan and Sieverts, *Z. anorg. Chem.*, 1933, **215**, 111.
[2] Colton and Wilkinson, *Chem. and Ind.*, 1959, 1314.
[3] Brukl and Ziegler, *Monatsh.*, 1933, **142**, 539.
[4] Woolf, *Quart. Rev.*, 1961, **15**, 372.

Rhenium pentabromide, made from bromine and rhenium at about 650°, is a bluish-green solid, melting readily to a similarly coloured liquid. The vapour is deep blue and the compound distils with little decomposition on gentle heating in a stream of bromine vapour. Moderate heating, or an attempt to distil it in a vacuum or in a nitrogen stream, leads, by rapid decomposition, to the tribromide. The pentabromide fumes in moist air and water causes instant hydrolysis which proceeds with the usual disproportionation of Re(v) compounds in these circumstances: $3Re^{V} \longrightarrow 2Re^{IV} + Re^{VII}$. We were unable to obtain a solution of the compound in any of several organic solvents, bromine being always liberated. This made it impossible to measure the magnetic susceptibility by the Evans nuclear magnetic resonance method.[5] It is hoped to obtain the susceptibility shortly by the Gouy method.

Rhenium tribromide is obtained from the pentabromide as dark brown crystals. Like rhenium trichloride, it is relatively involatile, but when strongly heated it gives a yellowish-green vapour. The vapour of the trichloride is green. It is stable in air, in acetone, alcohol, or ether to stable red solutions, but in water it is hydrolysed more quickly than the trichloride. Its absorption spectrum in acetone shows peaks at 750 and 440 mμ, resembling that of the trichloride (750 and 510 mμ). Hydrobromic acid produces a red solution with absorption peaks at 750 and 430 mμ, similar to that of a solution of the trichloride in hydrochloric acid (775 and 520 mμ) but so far we have been unable to isolate salts of $ReBr_4^-$ corresponding with those of the $ReCl_4^-$ ion. Rhenium tribromide has no absorption in the 1000 cm.$^{-1}$ region, indicating absence of Re=O bonds[6] and confirming the view that it was not an oxide bromide.

The compound Hagan and Sieverts thought was ReO_2Br_2 has now been shown to be rhenium oxide tetrabromide, $ReOBr_4$. It proves to be the main product of the following reactions: rhenium dioxide, heptoxide, or trioxide with bromine vapour; rhenium pentabromide, rhenium tribromide, or potassium hexabromorhenate(IV) (slight action only) with oxygen. Obtaining it from the heptoxide is surprising and is possibly due to decomposition of initially formed perrhenyl bromide to rhenium trioxide.[2] It is best prepared by passing bromine vapour over rhenium dioxide.

Rhenium oxide tetrabromide sublimes, with little decomposition, on gentle heating in a stream of bromine, but strong heating causes decomposition to the tribromide. It is stable in dry air but immediately hydrolysed by water to rhenium dioxide and a solution of perrhenic acid: $3Re^{VI} \longrightarrow 2Re^{VII} + Re^{IV}$.

Experimental.—Rhenium pentabromide. Metallic rhenium (from Johnson Matthey & Co. Ltd.) was placed in a porcelain boat in a wide Pyrex tube carrying at one end a narrow tube divided into sections by constrictions. Purified nitrogen, which had passed through bromine and then through concentrated sulphuric acid, was passed in at the wide end. The metal was heated to about 650° by an electric furnace. Despite these precautions some blue oxide bromide always appeared, presumably from oxygen associated with the metal. This was removed by sublimation to the far end of the narrow tube. Rhenium pentabromide from the reaction zone distilled into the narrow tube and was purified by gently distilling it from section to section in the bromine vapour. Finally nitrogen was passed over the sample to remove the excess of bromine vapour and the *pentabromide* was sealed off (Found: Re, 31·6; Br, 68·4. $ReBr_5$ requires Re, 31·8; Br, 68·2%).

Rhenium tribromide. Rhenium tribromide was made by heating the pentabromide in a stream of nitrogen or in a vacuum. It sublimed in a vacuum at about 350° c. (Found: Re, 43·6; Br, 56·6. $ReBr_5$ requires Re, 43·7; Br, 56·3%).

Rhenium oxide tetrabromide. Rhenium oxide tetrabromide was prepared by passing bromine vapour in nitrogen as carrier over dry rhenium dioxide at about 150°. The blue solid *product* was deposited in the cooler parts of the tube and was sublimed forward in the stream of bromine (Found: Re, 35·7; Br, 61·6. $ReBr_4$ requires Re, 36·8; Br, 63·2%).

[5] Evans, *J.*, 1959, 2003.
[6] Barraclough, Lewis, and Nyholm, *J.*, 1959, 3552.

Analyses. Samples were weighed in the sealed tubes used in the preparation which were then opened and washed out with alkaline hydrogen peroxide. Gentle heating dissolved the precipitated rhenium dioxide. The solution was diluted to precisely 100 ml., a small part (usually 1—5 ml.) was taken for determination of rhenium by the furil α-dioxime method; [7] bromine in the remaining solution was precipitated and weighed as silver bromide.

The oxidation state of rhenium was confirmed by hydrolysing the compounds in water, centrifuging off the precipitated dioxide, and determining the rhenium after dissolving it in a little alkaline hydrogen peroxide. The rhenium in the supernatant liquid from the hydrolysis (Re^{VII}) was also found. This gave the proportions of Re^{VII} and Re^{IV} formed by the hydrolysis of the compounds and fixed the oxidation state.

The author thanks Mr. F. Hudswell and Professor P. L. Robinson for their advice and encouragement, Mr. J. T. George for some experimental assistance, and the United Kingdom Atomic Energy Authority for a Harwell Research Fellowship.

CHEMISTRY DIVISION, ATOMIC ENERGY RESEARCH ESTABLISHMENT,
HARWELL, nr. DIDCOT, BERKS. [*Received, November 15th*, 1961.]

[7] Meloche, Martin, and Webb, *Analyt. Chem.*, 1957, **29**, 527.

---

397. *Clarification of Ambiguous Nuclear Magnetic Resonance Spectra by Double Irradiation.*

By R. J. ABRAHAM, R. FREEMAN, L. D. HALL, and K. A. MCLAUCHLAN.

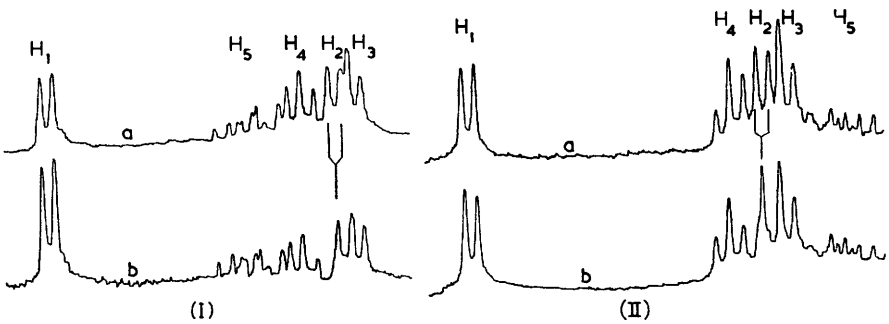
IN high-resolution proton magnetic resonance spectra, it is usually a simple matter to decide which pairs of protons in a molecule are coupled together by spin–spin interaction, because their resonance patterns have equal multiplet splittings. Occasionally such assignments are more difficult; for example, the resonance of one proton group may be obscured by overlying resonances from other protons, or two spin-coupling constants may be so nearly equal in magnitude that it is not possible to assign the spectrum unambiguously. Both of these problems can be resolved by the technique of spin decoupling. When a strong radiofrequency field is imposed near the resonance frequency of one proton group, the spin coupling to a second group can be destroyed. The resonance pattern of the second group, detected by means of the usual weak radiofrequency field, is then seen to collapse either to a single line or to the pattern generated by any residual spin couplings to other protons in the molecule. Elridge and Jackman [1] have demonstrated how the first problem can be solved by spin decoupling, so that a chemical shift may be obtained when one of the resonances is obscured by other lines. The present Note reports two instances of the use of the method in studying molecules that have two very nearly equal spin-coupling constants.

There are two methods by which nuclei may be decoupled in a field-sweep experiment: either the radiofrequency oscillator of the nuclear magnetic resonance spectrometer can be used to provide the strong field required for decoupling and a weak radiofrequency sideband to display the spectrum, or both the strong radiofrequency field and the weaker one can be sideband responses obtained by modulation of the spectrometer oscillator and main magnetic field, respectively. If the former method is used when, as in the examples below, the chemical shift between the nuclei to be decoupled is small, the spectrum is obscured because the unused sideband overlaps the spectrum. The second method has the advantage that the two modulation frequencies can be made sufficiently high to ensure that the unused sidebands do not overlap the spectrum. Further, since one sideband can be chosen arbitrarily, it is convenient to make one modulation frequency fixed (in this case 506·0 c./sec.) so that a tuned amplifier stage can be used in the lock-in

[1] Elridge and Jackman, *J.*, 1961, 859.

detector [2] which forms a part of the equipment for this experiment.[3] The rest of the apparatus consists of a Varian 60 mc./sec. V 4300 high-resolution spectrometer and two audiofrequency oscillators which provide the modulation frequencies. The spectra were recorded for ~5% solutions of the substances in chloroform, and the chemical shift of each proton was measured by the usual sideband technique. It is essential in double-irradiation experiments that the chemical shift be known accurately before double resonance is attempted.

The problems arose during a programme of investigation of some 1,2-*O*-isopropylidene-furanose derivatives (which will be described in detail elsewhere), *e.g.*, 3,6-anhydro-1,2-*O*-isopropylidene-5-*O*-tosyl-β-D-glucofuranose (I) and 3,6-anhydro-1,2-*O*-isopropylidene-α-D-glucofuranose (II). In their spectra assignment of the resonance peaks to the protons in the molecule is straightforward except for protons H_2 and H_3. These have similar



Normal (a) and decoupled (b) spectra of compounds (I) and (II).

chemical shifts and each gives a doublet of about 3·5 c./sec. splitting. (The coupling constant $J_{2,3}$ is too small to be observed.[4]) Clearly one of these protons is coupled to H_1 which gives a doublet resonance (3·5 c./sec. splitting) well separated from other lines. When H_1 is strongly irradiated it is the low-field doublet which collapses to a single line, and since spin–spin coupling is normally only observed between protons that are near neighbours in the molecule, this immediately identifies H_2. The relevant parts of the spectra are shown in the Figure with the normal spectrum above the decoupled one in each example, and with an indication of the collapse of the H_2 doublet. The modulation frequency differences were 83·0 c./sec. for (I) and 83·4 c./sec. for (II), in good agreement with the measured shifts. In neither instance was an effect produced by setting the modulation frequency difference equal to the chemical shift between H_1 and the high field doublet.

One of us (L. D. H.) thanks the Department of Scientific and Industrial Research for a maintenance grant.

BASIC PHYSICS DIVISION,
NATIONAL PHYSICAL LABORATORY, TEDDINGTON, MIDDLESEX.
CHEMISTRY DEPARTMENT,
THE UNIVERSITY, BRISTOL.
[*Received, November 23rd,* 1961.]

[2] Freeman, *Mol. Phys.*, 1960, **3**, 435.
[3] Freeman and Whiffen, *Mol. Phys.*, 1961, **4**, 321.
[4] Abraham, McLauchlan, Hall, and Hough, *Chem. and Ind.*, 1962, 213.

398 *The Acid Polysaccharide from the Green Seaweed,* Ulva lactuca.

By J. P. McKinnell and Elizabeth Percival.

Ulva lactuca, a green seaweed common to the British coastline and readily recognised by its broad leaf-like fronds, is commonly known as "sea lettuce." Preliminary structural examination of an alkaline-extracted polysaccharide [1] revealed a complex sulphated (16%) material consisting of rhamnose, xylose, glucose, and *ca.* 19% of uronic acid. The latter was characterised as D-glucuronic acid by the isolation, from a hydrolysate of the methylated polysaccharide, of methyl 2,3,4-tri-*O*-methyl-D-glucuronosidamide, but no evidence was advanced as to the mode of linkage of the uronic acid units in the polymer.

Supplies of this alga were harvested at Kames Bay, Millport, by Mr. Harry Powell and made available to the authors. After removal of the colouring matter, cold water extracted a sulphated polysaccharide similar in its constituent sugars and uronic acid to the alkaline-extracted material isolated by the earlier workers from this seaweed. Partial acid-hydrolysis of the polysaccharide, and separation of the neutral sugars and barium uronates on cellulose and on resin, led to the isolation of an aldobiouronic acid, $[\alpha]_D$ −22°. This had the same chromatographic and ionophoretic mobilities as the 4-*O*-β-D-glucuronosyl-L-rhamnose isolated from a partial hydrolysate of the water-soluble polysaccharide from *Acrosiphonia centralis*.[2] The difficulty of collecting large supplies of pure species of the latter weed and hence of obtaining sufficient quantities of the aldobiouronic acid to subject it to extensive purification may explain the smaller rotation (−6°) recorded for this acid.

Esterification and reduction of the present aldobiouronic acid to the disaccharide glycoside, followed by hydrolysis and characterisation of the derived glucose and rhamnose, confirmed the view that it comprised D-glucuronic acid and L-rhamnose. Periodate oxidation and methylation of the derived methyl D-glucosyl-L-rhamnoside provided proof that the aldobiouronic acid separated from the acid hydrolysate of the water-soluble polysaccharide from *U. lactuca* is indeed 4-*O*-β-D-glucuronosyl-L-rhamnose, the same acid as that reported to be present in similar hydrolysates of the polysaccharides from *A. centralis* [2] and *Enteromorpha compressa*.[3]

Experimental.—The dried weed was extracted several times with 80% aqueous acetone to remove the colouring matter which otherwise contaminated the cold water extract. Repeated cold-water extraction of the residual weed, followed by dialysis and concentration of the extracts, gave a stiff gel, which was isolated as an off-white flaky solid (6% of dry wt. of weed) on freeze-drying the gel. This had $[\alpha]_D$ −50° (*c* 1·1 in H_2O), ash 16, total SO_4^{2-} 18·2, N 0·43; uronic acid [4] 15·9%, and equiv. wt. 313. Chromatography of an acid hydrolysate indicated the presence of glucose, rhamnose, and a number of oligosaccharides. Prolonged acid-hydrolysis of the polysaccharide caused extensive degradation and failed to yield any indication of glucuronic acid or its lactone. An optimum yield of an aldobiouronic acid was obtained after hydrolysis with N-sulphuric acid at 100° for 5 hr. The barium uronates from such a hydrolysis were separated from the neutral sugars on a cellulose column (72% of neutral sugars and 17% of barium uronates were separated) and on Amberlite CG-45 resin (78% and 13%, respectively). In the former fractionation the neutral sugars were eluted with butan-1-ol half-saturated with water and the acids with butan-1-ol–acetic acid–water (2 : 1 : 1). In the resin-separation the neutral sugars were eluted with water, and the acids by gradient elution with formic acid (0 ⟶ 2N). From both methods a pure aldobiouronic acid constituting 75—78% of the acid fraction was separated. This had $[\alpha]_D$ −22° (*c* 1·2 in H_2O), $R_{Gal.\ Acid}$ 1·07,

[1] Brading, Georg-Plant, and Hardy, *J.*, 1954, 319.
[2] O'Donnell and Percival, *J.*, 1959, 2169.
[3] McKinnell and Percival, *J.*, in the press.
[4] Swenson, McCready, and Maclay, *Ind. Eng. Chem., Analyt.*, 1946, **18**, 290.

M_G 0·80 in borate buffer (pH 10) [5] (cf. 4-*O*-β-D-glucuronosyl-L-rhamnose, $R_{Gal.\ Acid}$ 1·07, M_G 0·80 [2]).

Hydrolysis and methanolysis of the aldobiouronic acid failed to yield any recognisable products, extensive degradation taking place. However, conversion of the acid into the methyl ester methyl glycoside,[2] followed by reduction to the disaccharide glycoside (82% yield) with potassium borohydride [6] and hydrolysis, gave a syrup containing glucose and rhamnose in the molar proportion [7] of 1 : 1. The former sugar was characterised by conversion into gluconic acid by the specific enzyme, glucose oxidase, and the rhamnose was isolated as the crystalline phenylosazone,[8] m. p. and mixed m. p. 190°. The glucose must have arisen from the reduction of the glycosidically linked glucuronic acid.

Measurement of the reduction of sodium metaperiodate [9] by the disaccharide glycoside gave a value of 3·10 moles per mole, indicating that the linkage is through position 2 or 4 of the rhamnose residue. Methyl 2- or 4-*O*-glucosylrhamnoside requires 3 mol. of periodate for complete oxidation, whereas methyl 3-*O*-glucosylrhamnoside consumes only 2 mol. The disaccharide glycoside was methylated three times with sodium hydroxide and dimethyl sulphate under nitrogen [2] and then with methyl iodide and silver oxide in dimethylformamide.[10] An aliquot part of the syrup derived after methanolysis was analysed by gas–liquid chromatography on an Apiezon M column at 150° [11] and shown to contain methyl 2,3,4,6-tetra-*O*-methyl-α and -β-glucoside, methyl 2,3-di-*O*-methyl-α- and -β-rhamnoside and *ca.* 5% of methyl 2,3,4-tri-*O*-methylrhamnoside. The identity of the methylated sugars was confirmed by acid hydrolysis and separation on 3MM chromatography paper by elution with butan-1-ol–ethanol–water (40 : 11 : 19). Crystalline 2,3,4,6-tetra-*O*-methyl-D-glucose, m. p. and mixed m. p. 84°, $[\alpha]_D$ +78° (*c* 1·0 in H_2O), and syrupy 2,3-di-*O*-methyl-L-rhamnose, $[\alpha]_D$ +42° (*c* 1·2 in H_2O), were separated. The latter had R_G and M_G mobilities identical with those of authentic 2,3-di-*O*-methyl-L-rhamnose run as a control in several solvents. Demethylation [12] gave only rhamnose. The quantity of tri-*O*-methylrhamnose was too small to be isolated and is considered to have arisen from inadvertent hydrolysis of a small proportion of the aldobiouronic acid and/or disaccharide before methylation.

The authors are grateful to Professor E. L. Hirst, C.B.E., F.R.S., for his interest and advice, to Dr. G. O. Aspinall for the gas chromatogram and to D.S.I.R. for a maintenance allowance (to J. P. McK.).

CHEMISTRY DEPARTMENT, UNIVERSITY OF EDINBURGH. [*Received, November 28th,* 1961.]

[5] Foster, *Chem. and Ind.*, 1952, 1050.
[6] Frush and Isbell, *J. Amer. Chem. Soc.*, 1956, **78**, 2844.
[7] Wilson, *Analyt. Chem.*, 1959, **21**, 1199.
[8] Freudenberg and Raschig, *Ber.*, 1929, **62**, 673.
[9] Aspinall and Ferrier, *Chem. and Ind.*, 1957, 1216.
[10] Kuhn, *Angew. Chem.*, 1955, **67**, 32.
[11] Bishop and Cooper, *Canad. J. Chem.*, 1960, **38**, 388.
[12] Allen, Bonner, Bourne, and Saville, *Chem. and Ind.*, 1958, **36**, 630.

---

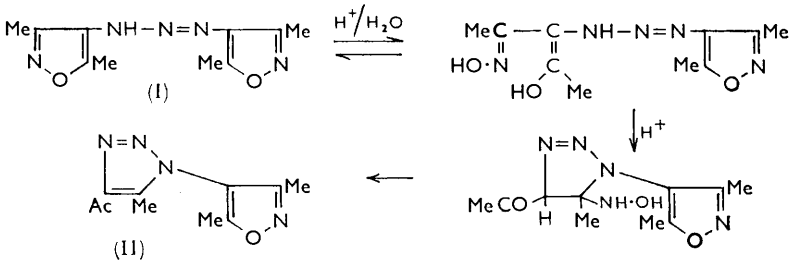
399. *Conversion of an Isoxazole into a Triazole.*

By A. J. BOULTON and A. R. KATRITZKY.

DIAZOTISATION of 4-amino-3,5-dimethylisoxazole [1] and treatment with potassium cyanide and cupric sulphate gave 4-acetyl-5-methyl-1-(3,5-dimethylisoxazol-4-yl)-1,2,3-triazole (II) instead of the expected 4-cyano-3,5-dimethylisoxazole. This structure was indicated by the infrared spectrum [0·2M-solution in $CHCl_3$, ν (C=O) at 1686 cm.$^{-1}$ (ε_A 350) and isoxazole ring bands [2] at 1652 (60), 1518 (55), 1484 (75), 1415 (210), 996 (45) and 872 cm.$^{-1}$ (30)], and by the proton resonance spectrum [four bands of equal intensity at τ 7·48, 7·67, 7·77, and 8·00 (in chloroform; τ 2·75)] which showed the presence of four methyl groups attached to sp^2-carbon atoms in different environments.

[1] Morgan and Burgess, *J. Chem. Soc.*, 1921, **119**, 699.
[2] Katritzky and Boulton, *Spectrochim. Acta*, 1961, **17**, 238.

The structure was proved by degradation of the isoxazole ring, followed by oxidation to 5-methyl-1,2,3-triazole-4-carboxylic acid, and by synthesis from 4-amino-3,5-dimethylisoxazole and 3-diazopentane-2,4-dione (a known triazole synthesis [3]).



The triazole (II) is probably formed through the diazoamino-compound (I); a possible route is shown, but the exact order of the steps is undetermined. Quilico and Musante [4] prepared 4-acetyl-5-methyl-1,2,3-triazole by boiling diazotised 4-amino-3,5-dimethylisoxazole with cupric sulphate and sulphuric acid: possibly this arose from an intermediate (II) by loss of the isoxazole ring.

Experimental.—*4-Acetyl-5-methyl-1-(3,5-dimethylisoxazol-4-yl)-1,2,3-triazole.* (a) From 4-Amino-3,5-dimethylisoxazole and nitrous acid. 4-Amino-3,5-dimethylisoxazole [1] (13·5 g.) was diazotised as described by Morgan and Burgess,[1] but with an equivalent amount of sulphuric acid in place of hydrochloric acid. A yellow tar separated. Potassium cyanide (9 g.) and cupric sulphate (0·2 g.) were added, the mixture was boiled for 1 hr. and diluted with water (100 ml.), and 100 ml. were distilled off (no organic material). The triazole (2·1 g., 16%) separated from the residue, after treatment with charcoal, as prisms, m. p. 141—143°; when recrystallised from water and sublimed at 135°/0·3 mm., it had $\lambda_{max.}$ 225 mμ (broad band) (ε 12,500) in water [Found: C, 54·5; H, 5·6; N, 25·3%. *M* (ebullioscopic in chloroform), 238. $C_{10}H_{12}N_4O_2$ requires C, 54·4; H, 5·5; N, 25·5%; *M*, 220]. The *2,4-dinitrophenylhydrazone* formed needles (from ethanol–chloroform), m. p. 244—246° (Found: C, 47·8; H, 4·3; N, 28·0. $C_{16}H_{16}N_8O_5$ requires C, 48·0; H, 4·0; N, 28·0%).

(b) From 4-amino-3,5-dimethylisoxazole and 3-diazopentane-2,4-dione. 3-Diazopentane-2,4-dione (diacetyldiazomethane) [3] (2·4 g.) was added to the aminoisoxazole (1·73 g.) in glacial acetic acid (10 ml.), and the mixture was heated at *ca.* 50° for 2 hr. and kept at room temperature for 2 days. Further diazo-compound (0·5 g.) was added; after 3 more days the crystals (1·34 g.) were filtered off. Dilution of the mother-liquor with water provided an additional 1·10 g. (total 72%). A sample, crystallised from benzene, had m. p. and mixed m. p. 141—143°. The infrared spectra of the two samples were identical.

(c) Degradation. The isoxazolyl-triazole (0·5 g.) in methanol (25 ml.) was shaken with platinum and hydrogen until 110 ml. (*ca.* 2 mol.) were absorbed. Filtration and evaporation gave a gum, which crystallised slowly. This was heated for 2 hr. with potassium permanganate (1·0 g.) and 2N-sulphuric acid (25 ml.) at 100°. The solution was decolorised with a little sodium hydrogen sulphite and continuously extracted with ether. 5-Methyl-1,2,3-triazole-4-carboxylic acid separated from the extracts: on recrystallisation from ether it had m. p. 211—212° (decomp.), on slow heating [lit., m. p. 214° (decomp.),[5] 220° (decomp.),[6] under similar conditions]. Its infrared spectrum was identical with that of an authentic sample [m. p. 218—219° (decomp.)] prepared from ethyl diazoacetoacetate.[6]

THE UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, November 29th*, 1961.]

[3] Wolff, *Annalen*, 1902, **325**, 139; 1912, **394**, 36.
[4] Quilico and Musante, *Gazzetta*, 1941, **71**, 327.
[5] Peratoner and Azzarello, *Gazzetta*, 1908, **38I**, 92.
[6] Wolff, *Annalen*, 1902, **325**, 134, 153.