NOTES.

The Synthesis of 2 : 4-Diamino-7-hydroxypteridine and its 6-Carboxylic Acid.

By T. S. Osdene and G. M. Timmis.

[Reprint Order No. 6036.]

2 : 4-Diamino-7-hydroxypteridine, the 4-amino-analogue of *iso*xanthopterin, was required for biological testing. The derived 6-carboxylic acid was unambiguously synthesised from 2 : 4 : 6-triamino-5-nitrosopyrimidine and a large excess of diethyl malonate in boiling 2-ethoxyethanol containing 2 mols. of sodium 2-ethoxyethoxide (4 hr.). If equimolecular quantities of the reactants were used, reaction was incomplete after 14 hr. The acid was decarboxylated on sublimation in a high vacuum at 340° and yielded 2 : 4-diamino-7-hydroxypteridine.

Experimental.—*2 : 4-Diamino-7-hydroxypteridine-6-carboxylic acid.* 2 : 4 : 6-Triamino-5-nitrosopyrimidine (3·1 g.) and diethyl malonate (25 ml.) were added to a solution of sodium (1·0 g.) in 2-ethoxyethanol (200 ml.), and the mixture was boiled under reflux for 4 hr. After cooling, the yellow precipitate was removed and the mother-liquors were evaporated to dryness to yield more material. These were combined and dissolved in boiling water (alkaline to litmus), and the hot solution was filtered into an excess of boiling 2N-hydrochloric acid. The resulting yellow precipitate (2·5 g.) was purified several times by dissolution in hot 2N-sodium carbonate which was filtered into boiling hydrochloric acid to yield *2 : 4-diamino-7-hydroxypteridine-6-carboxylic acid* as a yellow powder, m. p. >360° (Found, in material dried at 180° : C, 38·2; H, 2·65; N, 37·6. $C_7H_6O_3N_6$ requires C, 37·8; H, 2·7; N, 37·8%). The acid solution of the acid showed an intense blue fluorescence, and gave a single blue fluorescent spot on a paper chromatogram when viewed in ultraviolet light. The absorption spectrum in 0·1N-sodium hydroxide showed max. at 350 (ε 14,900), 260 (ε 11,300), and 226 mμ (ε 38,000).

2 : 4-Diamino-7-hydroxypteridine. The acid (0·4 g.) was sublimed at 340—360°/0·05 mm. The pale yellow sublimate (0·25 g.) was purified by dissolution in dilute ammonia solution, filtration, and boiling off the ammonia. On cooling, *2 : 4-diamino-7-hydroxypteridine* was obtained as pale yellow needles, m. p. >300° (Found, in material dried at 180° : C, 40·6; H, 3·35; N, 47·7. $C_6H_6ON_6$ requires C, 40·45; H, 3·4; N, 47·2%). The solution in ammonia

showed an intense violet fluorescence, and gave a single blue fluorescent spot on a paper chromatogram when viewed in ultraviolet light. The absorption spectrum in 0·1N-sodium hydroxide showed max. at 341 (ε 14,100), 255 (ε 10,900), and 224 mμ (ε 40,300).

We thank Dr. E. M. F. Roe for the absorption spectra. This investigation has been supported by grants to this Hospital and Institute from the British Empire Cancer Campaign, the Jane Coffin Childs Memorial Fund for Medical Research, the Anna Fuller Fund, and the National Cancer Institute of the National Institutes of Health, U.S. Public Health Service.

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The Reaction of Triethyl Phosphite with Phenylmagnesium Bromide.

By (MISS) M. H. MAGUIRE and G. SHAW.

[Reprint Order No. 5971.]

GILMAN and VERNON (*J. Amer. Chem. Soc.*, 1926, **48**, 1063) showed that the reaction of triphenyl phosphite and an excess of phenylmagnesium bromide gave a 60% yield of triphenylphosphine and 68% of phenol. Gilman and Robinson later (*Rec. Trav. chim.*, 1929, **48**, 328) reported (although no experimental details are given) that the reaction of triethyl phosphite with an excess of phenylmagnesium bromide gave 10% of triphenylphosphine oxide Ph_3PO, and that a similar reaction with trimethyl phosphite afforded 42% of methyldiphenylphosphine oxide, which the authors suggested might arise from rearrangement of methyl diphenylphosphinite $Ph_2P{\cdot}OMe$ (cf. Arbuzov, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 395).

The present work arose out of a need for a suitable preparation of certain phosphonous acids $R{\cdot}P(OH)_2$ and it was considered, in view of the above results, that the reaction of a Grignard reagent with an excess of triethyl phosphite might provide a satisfactory route to them. Initially, equimolar amounts of triethyl phosphite and phenylmagnesium bromide were brought together in ether: from the mixture were isolated diphenyl (6·7%), triphenylphosphine oxide (14%), diphenylphosphinic acid Ph_2PO_2H (7·2%), and phenylphosphonous acid $Ph{\cdot}P(OH)_2$ (15·3%), and some triethyl phosphite was recovered. The formation of the required phosphonous acid in this reaction was promising, and accordingly a further reaction was carried out with a 2 : 1 molar ratio of the phosphite to the Grignard reagent; however, the same products, diphenyl (5·3%), triphenylphosphine oxide (10%), diphenylphosphinic acid (20·1%), and phenylphosphonous acid (5·8%), were isolated; in addition a small amount of a neutral compound (C, 66·6; H, 5·25%) was obtained to which no simple structure could be assigned, and almost 1 mol. of triethyl phosphite was recovered.

Experimental.—Phenylmagnesium bromide (1 mol., prepared from 26 g. of bromobenzene and 4 g. of magnesium) in ether (34 ml.) was added dropwise during 20 min. with shaking to triethyl phosphite (27·6 g.) in ether (40 ml.) at room temperature; heat was evolved and a colourless dense oil separated. The mixture was boiled under reflux for 30 min., cooled, and treated gradually with crushed ice (12 g.) and hydrochloric acid (20 ml.; 5N); the aqueous layer was washed with ether (30 ml.). The organic extracts were combined, washed with water (2 × 30 ml.), dried (Na_2SO_4) and evaporated to a pale yellow oil (12·7 g.); this was distilled to give a colourless liquid (6·5 g.), b. p. 150—162° (a mixture of triethyl phosphite, b. p. 155°, and bromobenzene, b. p. 155°); the residue was distilled *in vacuo* and afforded fractions: (i) a clear liquid (0·6 g.) with a garlic odour, b. p. 40—60°/5 mm., (ii) an oil (1 g.), b. p. 120—125°/5 mm., (iii) an oil (1 g.), b. p. 120°/1·5 mm., and (iv) an oil (2·5 g.), b. p. 210—230°/1·5 mm.; fractions (ii), (iii), and (iv) crystallised; fractions (ii) and (iii) were combined, and the solid was collected and recrystallised from ethanol–water, to give diphenyl (1·7 g.), m. p. and mixed m. p. 70—71°. The material from fraction (iv), triphenylphosphine oxide (2·3 g.), recrystallised from ethanol–water as laths, m. p. 156—157° (Found: C, 77·7; H, 5·4. Calc. for $C_{18}H_{15}OP$: C, 77·7; H, 5·45%); Kosolapoff (*J. Amer. Chem. Soc.*, 1942, **64**, 2982) gives m. p. 152—153°. The aqueous solutions were combined, diluted to 300 ml., and extracted with ether (3 × 50 ml.);

evaporation of the dried extract gave an oil (4·5 g.) which partly crystallised; the solid, diphenylphosphinic acid (1·3 g.), separated from ethanol–water as laths, m. p. 188° (Found: C, 65·9; H, 5·0. Calc. for $C_{12}H_{11}O_2P$: C, 66·05; H, 5·1%); Malatesta (*Gazzetta*, 1947, **77**, 518) gives m. p. 190°. The aqueous solution was made alkaline with sodium carbonate (*ca.* 22 g.), and the precipitated magnesium carbonate filtered off. The filtrate was concentrated to 200 ml. and acidified with hydrochloric acid, diphenylphosphinic acid (0·3 g.) separating; the filtrate was extracted with ether (4 × 50 ml.); evaporation of the dried extract gave diphenylphosphinic acid (1 g.). The aqueous solution was concentrated to 100 ml., an oil separating; this was extracted by ether (3 × 50 ml.), and evaporation of the solvent gave a crystalline solid; phenylphosphonous acid (3·6 g.) separated from carbon tetrachloride–acetone–light petroleum as prisms, m. p. 83—84° (Found: C, 50·7; H, 4·95%; equiv., 140·5. Calc. for $C_6H_7O_2P$: C, 50·45; H, 4·85%; equiv., 142); Kosolapoff (*J. Amer. Chem. Soc.*, 1950, **72**, 4291) gives m. p. 86°. The aqueous solution was finally evaporated to dryness and the solid residue was exhaustively extracted successively with ether and dry ethanol, but evaporation of the extracts gave in each case only a trace of gum.

We thank Dr. E. Challen for the microanalyses and the C.S.I.R.O. for a maintenance grant (to M. H. M.).

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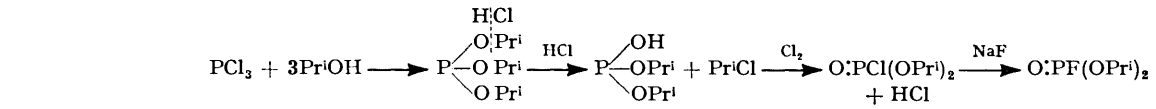
Esters containing Phosphorus. Part XII. Esters of Phosphorofluoridic Acid.*

By H. GOLDWHITE and B. C. SAUNDERS.

[Reprint Order No. 5998.]

DI*iso*PROPYL PHOSPHOROFLUORIDATE has been prepared in good yield by a process depending upon the reactions outlined below (McCombie and Saunders, *Nature*, 1946, **157**, 287; Saunders *et al.*, B.P. 601,210; Saunders and Stacey, *J.*, 1948, 695). American workers (U.S.P. 2,409,039) have similarly used the process starting with as much as 212 lb. of *iso*propanol. For small-scale work, however, chlorination of the hydrogen phosphite can be conveniently carried out by *N*-chlorosuccinimide; this method has the advantage that none of the products of the reaction is acidic (Kenner, Todd, and Weymouth, *J.*, 1952, 3675). We have shown that pure di*iso*propyl phosphorochloridate



can be obtained from di*iso*propyl hydrogen phosphite in 82% yield. It is also possible to prepare di*iso*propyl phosphorofluoridate without isolating the corresponding phosphorochloridate and thus the preparation can be run virtually as a " one-stage " process.

Di*cyclo*hexyl phosphorofluoridate is more toxic, and more stable to hydrolysis, than di*iso*propyl phosphorofluoridate. It is not easily obtained, however, by Saunders and Stacey's process, but we had prepared it by the action of phosphoryl dichlorofluoride on *cyclo*hexanol (Chapman and Saunders, *J.*, 1948, 1010): $POCl_2F + 2C_6H_{11}\cdot OH = (C_6H_{11}O)_2POF + 2HCl$. We have now shown that the action of *N*-chlorosuccinimide on di*cyclo*hexyl hydrogen phosphite followed by fluorination provides a convenient alternative preparation, and di*cyclo*hexyl phosphorofluoridate is now readily available. Most esters of phosphorofluoridic acid hitherto described in this series of papers can be prepared readily on a small scale in this way. Chlorination by *N*-chlorosuccinimide is more satisfactory than by sulphuryl chloride (Atherton, Howard, and Todd, *J.*, 1948, 1106) since an acid medium is produced by the latter reagent. By the former method it is possible to prepare phosphorofluoridates which contain unsaturated radicals, *e.g.*, diallyl phosphorofluoridate. In particular, compounds which decompose in the presence of acid on distillation are now easily obtained.

* Part XI, *J.*, 1953, 2115.

Experimental.—Diisopropyl phosphorochloridate. To a solution of di*iso*propyl hydrogen phosphite (0·1 mole) in dry carbon tetrachloride, *N*-chlorosuccinimide (0·1 mole) was added in portions of 0·5 g., with shaking and occasional cooling. The solution was then cooled to −5°, and the precipitated succinimide filtered off. Carbon tetrachloride was removed from the filtrate under reduced pressure, and the residue was fractionated. The product (17·5 g., 82%) boiled at 94—95°/14 mm. (McCombie, Saunders, and Stacey, *J.*, 1945, 380, give b. p. 95°/14 mm.).

Cognate preparations of $(RO)_2POCl$.

R	Yield (%) from $P(OR)_2(OH)$	B. p./mm.	R	Yield (%) from $P(OR)_2(OH)$	B. p./mm.
Me	85%	54·5°/2	CH_2:CH·CH_2 ...	38%	89—90°/0·9
Et	87·5%	93°/18	–CHMe·CO_2Et ...	75%	158—160°/1

Two procedures for the preparation of the esters of phosphorofluoridic acid were developed—a general one applicable to most alcohols and a special one adopted for *cyclo*hexanol.

Esters of phosphorofluoridic acid. (i) General procedure. To a vigorously stirred solution of the dry redistilled alcohol (0·3 mole) in dry carbon tetrachloride (30 ml.) a solution of redistilled phosphorus trichloride (0·1 mole) in carbon tetrachloride (20 ml.) was slowly added. After the addition, hydrogen chloride was expelled by refluxing the solution for 1 hr. and then by drawing dry air under reduced pressure through it for 2 hr. Solvent was added to replace that lost by evaporation, and the hydrogen phosphite was chlorinated by the addition in small portions (0·2 g.) of *N*-chlorosuccinimide (0·1 mole) with vigorous shaking and occasional cooling. The solution was then cooled to 5°, and the succinimide filtered off and washed with cold carbon tetrachloride. To the filtrate was added dry sodium fluoride (0·5 mole), and the mixture heated under reflux with vigorous stirring for 3 hr. The solids were filtered off, and the filtrate was dried (Na_2SO_4). Low-boiling liquids were removed by warming under reduced pressure. The residue was fractionated at low pressure in dry nitrogen to yield pure phosphorofluoridate.

Phosphorofluoridates, $(RO_2)_2POF$, *prepared as above.*

R	Yield (%) (from PCl_3 used)	B. p./mm.	F (%) * Found	F (%) * Calc.
Me	35	149—150°/760	14·70	14·82
Et	42	74·5—75·5/20	12·15	12·18
$CH_2F·CH_2$	70	101—102/0·8	29·60	29·70
$CH_2Cl·CH_2$	82	159—160/23	8·51	8·45
Pr^i	76	83/22	10·22	10·32
CH_2:CH·CH_2	37	99—100/23	10·90	10·60
Me·CH(CO_2Et)	47	128—130/1·0	6·60	6·33
$CHMe_2·CH_2·CHMe$	54·5	105—106/1·0	7·10	7·09

* The normal analytical procedure (Chapman, Heap, and Saunders, *Analyst*, 1948, **73**, 434—441) was used throughout except for difluoroethyl phosphorofluoridate (R = $CH_2F·CH_2$). Here the method was modified by using enough sodium to provide 5-fold excess for the total fluorine content, and by refluxing the solution of the phosphorofluoridate and sodium ethoxide in ethanol for 3 hr. to ensure hydrolysis of the C–F as well as of the P–F links.

(ii) Di*cyclo*hexyl phosphorofluoridate. Phosphorus trichloride (13·75 g.) in carbon tetrachloride (20 ml.) was slowly added to dry distilled *cyclo*hexanol (30 g.). A stream of dry air was drawn through the solution during the addition to ensure thorough mixing and removal of hydrogen chloride. The solution was then heated under reflux for 1½ hr. and solvent and other low-boiling liquids were removed on a water-bath under reduced pressure and then at 100°/0·5 mm. The residual crude hydrogen phosphite was then dissolved in dry benzene (50 ml.) and chlorinated by addition of *N*-chlorosuccinimide (13·35 g.) in portions as described in the previous experiment. After cooling, the succinimide was filtered off, and the filtrate was heated to 60—70° with dry ammonium fluoride (18 g.) for 4 hr., with vigorous stirring. The product was shaken with water (100 ml.) and then twice with aqueous sodium hydroxide (50 ml.; 10%). The benzene solution was finally washed with water (2 × 50 ml.) and dried (Na_2SO_4). The benzene was removed under reduced pressure, and the residue fractionated in dry nitrogen, giving the pure di*cyclo*hexyl phosphorofluoridate (14 g., 52%), b. p. 125—128°/0·6 mm. (Found: F, 7·0. Calc. for $C_{12}H_{22}O_3FP$: F, 7·1%).

We are grateful to the D.S.I.R. for a maintenance grant (to H. G.).

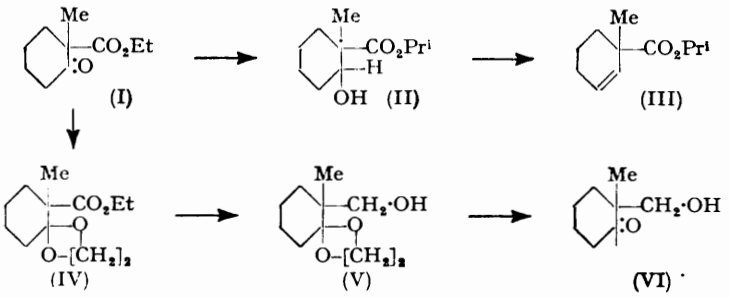
UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, December 23rd*, 1954.]

Possible Intermediates for the Synthesis of Simple Analogues of Steroids.

By EDWARD R. CLARK and P. F. EPSTEIN.

[Reprint Order No. 51007.]

SOME reactions of the readily available ethyl 1-methyl-2-oxo*cyclo*hexane-1-carboxylate (I) have been examined with a view to the synthesis of simple analogues of biologically active steroids. Meerwein–Pondorf reduction yielded *iso*propyl 2-hydroxy-1-methyl*cyclo*hexane-1-carboxylate in 74% yield in 24 hr. [shorter periods yielded mixtures with the corresponding ethyl ester which was not readily separable by distillation (cf. Robinson and Walker, *J.*, 1937, 60)]. The derived methoxy-ester gave the methoxy-acid on alkaline hydrolysis and the methoxy-alcohol on Bouveault–Blanc reduction.



The hydroxy-ester (II) was best (20%) converted into the *cyclo*hexene derivative (III) by treatment with phosphorus pentachloride in ether and subsequent heating with γ-collidine, which gave also a chlorine-containing compound believed to be essentially the chloro-ester though this could not be dehydrohalogenated by treatment with quinoline. The difficulty experienced in this dehydration and the comparative "stability" of the chloro-compound suggest some degree of rigidity in the ring structure preventing the adoption of the optimum conformation for ready elimination.

The *cyclo*hexene derivative (III) was readily brominated by *N*-bromosuccinimide. The crude product, which was not purified, did not yield the expected *iso*propyl 4-*p*-methoxyphenyl-1-methyl*cyclo*hex-2(or 3)-ene-1-carboxylate on treatment with *p*-methoxyphenylmagnesium bromide, but 47% of *iso*propyl 4-bromo-1-methyl*cyclo*hexene-1-carboxylate was isolated.

2-Hydroxymethyl-2-methyl*cyclo*hexanone (VI) has been prepared from our ester (I) *via* the ethylenedioxy-derivatives (IV and V) (cf. Buckta and Wolfrum, *Annalen*, 1953, **580**, 132) : sodium and alcohol give yields of the alcohol (V) comparable with those obtained by using lithium aluminium hydride. The ethylenedioxy-group was hydrolysed by use of dilute phosphoric acid.

Experimental.—iso*Propyl* 2-*hydroxy*-1-*methyl*cyclo*hexane*-1-*carboxylate*. Ethyl 1-methyl-2-oxo*cyclo*hexane-1-carboxylate [Chatterjee and Roy, *J. Indian Chem. Soc.*, 1943, **20**, 329 (Found : C, 65·4; H, 8·7. Calc. for $C_{10}H_{16}O_3$: C, 65·2; H, 8·7%); *semicarbazone*, m. p. 161° (Found : C, 54·7; H, 7·6; N, 16·7. $C_{11}H_{19}O_3N_3$ requires C, 54·8; H, 7·9; N, 17·4%)] (106·6 g.) and *iso*propyl alcohol (600 c.c.) were added to freshly prepared aluminium *iso*propoxide (120·4 g.), and the reduction carried out in the usual manner for 24 hr. The alcohol was distilled off under reduced pressure, the residue decomposed with a slight excess of hydrochloric acid, and the product extracted with ether. Distillation gave iso*propyl* 2-*hydroxy*-1-*methyl*cyclo*hexane*-1-*carboxylate* (86 g.), b. p. 108—110°/11 mm. (Found : C, 66·3; H, 10·0. $C_{11}H_{20}O_3$ requires C, 66·0; H, 10·0%).

iso*Propyl* 2-*methoxy*-1-*methyl*cyclo*hexane*-1-*carboxylate*. The foregoing hydroxy-ester (20 g.) in sodium-dried ether (20 c.c.) was slowly added to powdered sodium (2·5 g.) in ether (100 c.c.), and the mixture heated on the steam-bath and stirred until all the sodium had reacted (2—3 hr.). Methyl iodide (17·1 g.) was added to the refluxing solution and the mixture stirred on the steam-bath for a further 3 hr. After filtration, distillation yielded the 2-*methoxy-ester* (13 g.), b. p. 97—102°/9—10 mm. (Found : C, 67·25; H, 10·45. $C_{12}H_{22}O_3$ requires C, 67·3; H, 10·3%).

2-Methoxy-1-methylcyclohexane-1-carboxylic acid. The methoxy-ester (50·8 g.), when heated on the steam-bath for 6 hr. with 10% alcoholic potassium hydroxide (200 c.c.), gave the *methoxy-acid* (22·5 g.), m. p. 89° (from 25% aqueous alcohol) (Found : C, 62·7; H, 9·2. $C_9H_{16}O_3$ requires C, 62·8; H, 9·3%), and, from the mother-liquors, *2-hydroxy-1-methylcyclohexane-1-carboxylic acid* (3·4 g.) (Found : C, 60·4; H, 9·2. $C_8H_{14}O_3$ requires C, 60·75; H, 8·85%).

1-Hydroxymethyl-2-methoxy-1-methylcyclohexane. Sodium (31·2 g.), in large pieces, was added as rapidly as possible to a solution of *iso*propyl 2-methoxy-1-methyl*cyclo*hexane-1-carboxylate (47·7 g.) in alcohol (400 c.c.), cooled in ice-water. The mixture was then stirred and heated on the steam-bath until dissolution of the sodium was complete (2—3 hr.). Water was added, the alcohol distilled off, and the resulting oil extracted with ether. Distillation yielded *1-hydroxymethyl-2-methoxy-1-methylcyclohexane* (20·8 g.), b. p. 97—103°/12 mm. (Found : C, 68·7; H, 11·7. $C_9H_{18}O_2$ requires C, 68·35; H, 11·4%). This gave a *p-nitrobenzoate*, m. p. 73—74° (Found : C, 62·85; H, 6·45; N, 4·55. $C_{16}H_{21}O_5N$ requires C, 62·55; H, 6·85; N, 4·55%).

Dehydration of iso*propyl 2-hydroxy-1-methylcyclohexane-1-carboxylate.* The hydroxy-ester (30 g.) was added during 25 min. to a stirred suspension of phosphorus pentachloride (32 g.) in dry ether (120 c.c.), at 0—10°. The mixture was heated under reflux for 1 hr., decomposed with ice, and extracted with ether in the usual manner. Distillation yielded a fraction, b. p. 80—115°/10 mm. (15 g.), which was heated at 160° for 10 min. with freshly distilled collidine. The cooled mixture was treated with dilute sulphuric acid and the oil extracted with ether. Distillation yielded iso*propyl 1-methylcyclohex-2-ene-1-carboxylate* (5·2 g.), b. p. 77—78°/11 mm. (Found : C, 72·2; H, 10·0. $C_{11}H_{18}O_2$ requires C, 72·5; H, 9·9%), and an oil (4·3 g.), b. p. 113/11 mm., consisting mainly of *iso*propyl 2-chloro-1-methyl*cyclo*hexene-1-carboxylate (Found : C, 61·8; H, 9·4; Cl, 14·95. Calc. for $C_{11}H_{19}O_2Cl$: C, 60·4; H, 8·7; Cl, 16·2%).

Poorer yields of the *cyclo*hexene (III) were obtained by using phosphorus tribromide and pyridine, and by distillation of the phosphate ester obtained by the action of phosphorus pentoxide on the alcohol. Potassium hydrogen sulphate and activated alumina both failed to effect the dehydration.

Bromination of iso*propyl 1-methylcyclohex-2-ene-1-carboxylate and attempted Grignard reaction.* The unsaturated ester (6·5 g.), *N*-bromosuccinimide (6·2 g.), and carbon tetrachloride (40 c.c.) were heated under reflux under nitrogen for 2½ hr., then filtered and evaporated. An ethereal solution (30 c.c.) of the residue, cooled in ice, was treated with *p*-methoxyphenylmagnesium bromide [from *p*-bromoanisole (6 g.) and magnesium (0·78 g.) in ether (20 c.c.)] during 2 hr. and the mixture stirred in ice for a further 30 min. Next morning, no Grignard reagent remained (test with Michler's ketone). Working up in the usual manner yielded iso*propyl 4-bromo-1-methylcyclohex-2-ene-1-carboxylate* (4·4 g.), b. p. 65—67°/0·1 mm. (Found : C, 50·35; H, 6·7; Br, 30·3. $C_{11}H_{17}O_2Br$ requires C, 50·6; H, 6·5; Br, 30·7%).

Ethyl 2 : 2-ethylenedioxy-1-methylcyclohexane-1-carboxylate. Ethyl 1-methyl-2-oxo*cyclo*hexane-1-carboxylate (20 g.), ethylene glycol (8 g.), a crystal of toluene-*p*-sulphonic acid, and dry benzene (100 c.c.) were refluxed under a water-separator, until no more water separated (14 hr.). The benzene solution was washed with sodium carbonate solution, and water, and dried (Na_2SO_4). Distillation yielded the 2 : 2-ethylenedioxy-ester (22·3 g.), b. p. 136°/16 mm. (Found : C, 64·0; H, 8·9. Calc. for $C_{12}H_{20}O_4$: C, 63·15; H, 8·8%). Repeated redistillation failed to yield a pure product with a closer analysis for carbon : probably some ester interchange took place.

2 : 2-Ethylenedioxy-1-hydroxymethyl-1-methylcyclohexane. The foregoing ester (20 g.) was reduced with absolute alcohol (200 c.c.) and sodium (12·5 g.) as described above. The 2 : 2-ethylenedioxy-alcohol (14 g.), b. p. 136°/14 mm., was obtained (Found : C, 64·35; H, 9·6. Calc. for $C_{10}H_{18}O_3$: C, 64·5; H, 9·75%).

1-Hydroxymethyl-1-methylcyclohexan-2-one. The foregoing alcohol (10 g.) was heated under reflux for 2 hr. with a 5% aqueous solution (35 c.c.) of syrupy phosphoric acid. Ether-extraction, etc., yielded 1-hydroxymethyl-1-methyl*cyclo*hexan-2-one (5·7 g.), b. p. 103—104°/11 mm. (Found : C, 67·7; H, 10·1. Calc. for $C_8H_{14}O_2$: C, 67·6; H, 9·85%) [*2 : 4-dinitrophenylhydrazone*, m. p. 73° (Found : C, 52·2; H, 5·55; N, 17·7. $C_{14}H_{18}O_5N_4$ requires C, 52·2; H, 5·6; N, 17·4%)].

One of us (P. F. E.) acknowledges the receipt of a grant from the D.S.I.R. We are indebted to Mrs. Y. Richards and Miss M. Clarke of the Microanalytical Laboratory for the analyses.

THE UNIVERSITY, LEEDS. [*Received, December 28th*, 1954.]

*Hydrazine. Part XI.** N-*Methyl-aldazinium and -ketazinium Chlorostannates derived from Methylhydrazine.*

By M. LAMCHEN and A. M. STEPHEN.

(Reprint Order No. 51017.)

IT was shown in Part IX * that condensation of acetone with methylhydrazine in presence of hydrochloric acid and stannic chloride afforded the chlorostannate of *N*-methyldimethyl ketazine, not a pyrazolinium derivative as when hydrazine was used instead of methylhydrazine. We have extended this reaction by substituting ethyl methyl ketone, diethyl ketone, methyl *n*-propyl ketone, acetophenone, and a number of aldehydes for acetone, whereupon the corresponding *N*-methylaldazinium salts and one *N*-methylketazinium salt have been obtained.

The annexed Table indicates the nature of the chlorostannates formed by reaction of carbonyl compounds with methylhydrazine in methanol containing aqueous hydrochloric acid and a small excess of stannic chloride. The aldazinium salts crystallised readily within a few minutes in the cold, but the product obtained from ethyl methyl ketone

N-*Methyl-aldazinium and -ketazinium chlorostannates*, $[R{:}N{\cdot}\overset{+}{N}Me{:}R]_2SnCl_6^{2-}$.

Compound : * R =	M. p.	Formula	(Found %) Cl	(Found %) N	Required (%) Cl	Required (%) N
(1) CMeEt †	138—139°	$(C_9H_{19}N_2)_2SnCl_6$	33·2	8·8	33·2	8·7
(2) $C_6H_5{\cdot}CH$	205—206	$(C_{15}H_{15}N_2)_2SnCl_6$	27·1	7·0	27·4	7·2
(3) $C_6H_5{\cdot}CH{:}CH{\cdot}CH$	197 (decomp.)	$(C_{19}H_{19}N_2)_2SnCl_6$	23·8	6·7 ‡	24·15	6·4
(4) p-$C_6H_4(OMe){\cdot}CH$	215—216	$(C_{17}H_{19}O_2N_2)_2SnCl_6$	24·0	6·2	23·7	6·2
(5) 2 : 4-$C_6H_3(OH)_2{\cdot}CH$	*ca.* 230	$(C_{15}H_{15}O_4N_2)_2SnCl_6$	23·5	6·5 ‡	23·5	6·2
(6) 3 : 4-$C_6H_3(OMe)(OH){\cdot}CH$	*ca.* 180	$(C_{17}H_{19}O_4N_2)_2SnCl_6$	22·0	6·4 ‡	22·15	5·8
(7) 3 : 4-$C_6H_3(OMe)_2{\cdot}CH$	225 (decomp.)	$(C_{19}H_{23}O_4N_2)_2SnCl_6$	20·9	5·4 ‡	20·9	5·5

* Appearance : (1) Colourless squat prisms; (2)—(5) microcrystalline, and pale yellow, vermilion, bright yellow and deep yellow, respectively; (6) and (7) deep yellow powders; (5) and (6) became blood-red in conc. aq. NaOH, forming a yellow solution on dilution.

† Reactants heated for 15 min. under reflux.

‡ Estimated by Dumas's method; compound not decomposed quantitatively by boiling with aqueous hydrochloric acid.

separated from solution only after storage for one week at — 10°. No satisfactory compounds could be prepared from acetaldehyde, propaldehyde, crotonaldehyde, or the ketones, other than ethyl methyl ketone, named above. When salicylaldehyde was used, salicylaldazine methochloride was precipitated instead of the corresponding chlorostannate; its ease of formation is unexpected in view of difficulties encountered in preparing salicylaldazine hydrochloride (Mrs. E. G. Sohn, personal communication; cf. Part X, *loc. cit.*).

In general, the salts are hydrolysed readily in aqueous acid solution, forming the aldehyde or ketone, as shown by reaction with 2 : 4-dinitrophenylhydrazine. Gelatinous tin hydroxide is formed when the chlorostannates are boiled with water. Although the products from vanillin and veratraldehyde dissolved in dilute hydrochloric acid, the aldehydes could not be driven out by evaporating the solution to small bulk; on cooling, the aldazinium salts were reprecipitated.

The observation (Part IX) that the use of phenylhydrazine in place of hydrazine gave, with boiling acetone, hydrochloric acid, and stannic chloride, an *N*-substituted pyrazolinium chlorostannate led us to repeat this reaction with other ketones : ethyl methyl, methyl *n*-propyl, and di-*n*-propyl ketone afforded substituted indoles and ammonium chlorostannate, and methyl *iso*propyl and di*iso*propyl ketone gave the indoleninium and ammonium chlorostannates.

Experimental.—Methods of analysis were as described in Parts VI and X (*locc. cit.*). The nitrogen values given in the Table were calculated from the methylhydrazine content where this could be determined; combustion (Dumas) was resorted to if the salt was not completely decomposed by dilute acid.

* Parts VI, IX, and X, *J.*, 1953, 3445; 1954, 2429; 1955, 1753.

Methylhydrazine hydrochloride, prepared from the sulphate, crystallised from methanol as glistening prisms, m. p. 137° (sintering at 131°) (Found, in material dried at 80° *in vacuo*: Cl, 52·9; CH_6N_2, 45·5. Calc. for CH_6N_2,HCl + CH_6N_2,2HCl: Cl, 53·0; CH_6N_2, 45·7%).

Salicylaldazine Methochloride.—Addition of salicylaldehyde (4 c.c.) in methanol to methylhydrazine (0·3 g.) in methanol containing a small excess of aqueous hydrochloric acid caused precipitation within a few minutes of the above *methochloride* as canary-yellow, glistening plates, m. p. 204° (decomp.) (Found, on material dried at 80° *in vacuo*: Cl, 12·1; CH_6N_2, 15·4. $C_{15}H_{15}O_2N_2Cl$ requires Cl, 12·2; CH_6N_2, 15·8%). The same compound was formed when stannic chloride (0·2 c.c.) was added before the salicylaldehyde. The methochloride became deep-red in contact with concentrated aqueous alkali, the colour changing to yellow on dilution with water.

Bis-(2 : 3 : 3-*trimethylindoleninium*) *hexachlorostannate.* To phenylhydrazine hydrochloride (3·7 g.) in methyl *iso*propyl ketone (30 c.c.) were added stannic chloride (2 c.c.) and concentrated hydrochloric acid (1 c.c.), and the solution was heated on the water-bath under reflux. Colourless crystals were deposited within 20 min., and after 7 hr. the mixture was cooled and the solid (7·0 g.) collected. Recrystallisation from dilute hydrochloric acid removed ammonium chlorostannate and afforded the above-named *salt* as nearly white prisms, m. p. 229° [Found, in material dried at 100° *in vacuo*: Cl, 32·6; N, 4·2. $(C_{11}H_{14}N)_2SnCl_6$ requires Cl, 32·65; N, 4·3%]. When a solution of the chlorostannate was made alkaline, the base was liberated; this was characterised as the picrate, m. p. 161° (lit. 158°).

Bis-(3 : 3-*dimethyl*-2-iso*propylindoleninium*) *hexachlorostannate.* By an essentially similar method di*iso*propyl ketone afforded crystals of ammonium chlorostannate embedded in a viscous yellow oil. The mixture was made alkaline and steam-distilled, yielding 3 : 3-dimethyl-2-*iso*propylindolenine after extraction of the steam-distillate with light petroleum (b. p. 40—60°); this was converted in the usual way into a *chlorostannate*, which formed prisms, m. p. 174° (red melt) after recrystallisation from dilute hydrochloric acid [Found, in material dried at 80° *in vacuo*: Cl, 30·0; N, 4·3. $(C_{13}H_{18}N)_2SnCl_6$ requires Cl, 30·1; N, 4·0%]. Both the indolenine and the salt were identical with samples prepared by Plancher's method (*Ber.*, 1898, **31**, 1498) from di*iso*propyl ketone phenylhydrazone.

UNIVERSITY OF CAPE TOWN. [*Received, December 30th*, 1954.]

Some Reactions of cyclo*Propane, and a Comparison with the Lower Olefins. Part II.* Some Platinous–*cyclo*Propane Complexes.*

By C. F. H. TIPPER.

[Reprint Order No. 6013.]

OLEFINS act as ligands in complexes with silver, cuprous, mercuric, and platinous salts (Keller, *Chem. Rev.*, 1941, **28**, 229). If the *cyclo*propane ring has some double-bond character, this compound might possibly form similar complexes. Solid silver nitrate, mercuric acetate, and cuprous chloride showed no evidence of complex formation in the presence of liquid *cyclo*propane at room temperature (cf. propylene; Francis, *J. Amer. Chem. Soc.*, 1951, **73**, 3709). However, when a dilute solution of chloroplatinic acid in acetic anhydride was treated with *cyclo*propane at room temperature, roughly four moles of gas per mole of acid were very rapidly absorbed, and a brown solid separated which gave reactions to be expected of a platinous–*cyclo*propane complex. When propylene was used, only platinous chloride was precipitated, and when shaken with aqueous potassium chloroplatinite *cyclo*propane was absorbed very slowly if at all.

The brown powder, dried *in vacuo*, rapidly absorbed up to ~4% of its weight of water from the atmosphere, but no more. It was very slightly soluble in water, the suspension being acid and titratable with sodium hydroxide solution. When it was boiled with water, platinum was rapidly formed. Addition of cold aqueous potassium cyanide led to a brisk evolution of *cyclo*propane. The solid dissolved in warm (~60°) pyridine or styrene, gas being evolved, and in quinoline to give a red-brown solution. It dissolved slowly in 10N-hydrochloric acid, and was moderately soluble in ethyl alcohol and slightly soluble in

* Part I, *J.*, 1955, 713.

ether, acetone, chloroform, and carbon tetrachloride. On separation from the organic liquid a substance of empirical formula $PtCl_2,C_3H_6$ was obtained. By analogy with the olefin complexes the molecular formula is presumably $(PtCl_2,C_3H_6)_2$. Analysis of the brown powder, together with the acid nature of its aqueous suspension, gives some indication that it is a mixture of the above complex with $HPtCl_3,C_3H_6,H_2O$ (analogous to Zeise's acid). However, it has not been possible to isolate this compound, if, indeed, it exists.

The reaction of pyridine and the "mixture" *in vacuo* gave a white compound $(C_5H_5N)_2PtCl_2,C_3H_6$. This decomposed in boiling water to give platinum, and dissolved in warm 10N-hydrochloric acid, but appeared to be more stable than the other two complexes in that potassium cyanide solution at 30—40° released *cyclo*propane only slowly, and no gas was evolved with warm pyridine, styrene, or aqueous sodium nitrite.

The fact that only *cyclo*propane was evolved when the complexes were treated with cyanide strongly suggests that the three-membered ring is intact in these molecules. The infrared spectrum of *cyclo*propaneplatinous chloride includes two very strong peaks at 3·27 and 3·35 μ, which might be *cyclo*propane C–H vibration bands shifted slightly from 3·23 and 3·32 μ (Stabley, *J. Amer. Chem. Soc.*, 1954, **76**, 3604) owing to complex formation. The existence of only two C–H absorptions, if not due to inadequate resolution by the spectrometer, suggests that the platinum atom is bound equally to all three carbon atoms.* However, whatever their detailed molecular structure, the actual existence of these substances strongly supports the view of both Walsh (*Trans. Faraday Soc.*, 1949, **45**, 179) and of Coulson and Moffitt (*Phil. Mag.*, 1949, **40**, 1) that there is considerable delocalisation of the electrons of the *cyclo*propane ring.

Experimental.—(Microanalyses were by Mr A. S. Inglis, of the Department of Organic Chemistry.)

*cyclo*Propane (from a cylinder) was passed for 2 hr. through a solution of commercial "platinum chloride" (1 g.) in 15—20 ml. of "AnalaR" acetic anhydride; the red colour soon darkened and a brown powder began to be precipitated. The whole was left overnight, and the precipitate filtered off, washed with acetic anhydride, and dried *in vacuo* (yield 0·1—0·15 g.) [Found: Pt (ash), 57·8; C, 11·1; H, 2·3; Cl, 25·0. Calc. for $C_3H_9OCl_3Pt$: Pt, 53·8; C, 9·9; H, 2·5; Cl, 29·3%. Calc. for $C_3H_6Cl_2Pt$: Pt, 63·3; C, 11·7; H, 2·0; Cl, 23·0%]. The powder decomposed during several months, going grey-green ($PtCl_2$) and then black. Addition of aqueous potassium cyanide *in vacuo* gave a gas condensable in liquid nitrogen. It burned over copper oxide to give approx. 3 vols. of carbon dioxide, and was completely absorbed by 85% sulphuric acid but unaffected by a solution of mercuric sulphate in 22% sulphuric acid. The gas was therefore *cyclo*propane (*e.g.*, see Brooks, Murdock, and Zahn, *Analyt. Chem.*, 1948, **20**, 62).

cyclo*Propaneplatinous chloride.* The dried product from the above preparation was shaken with 2—3 ml. of acetone–ether (1 : 1), and the solid collected, washed with 1—2 ml. of the liquid, then with acetic anhydride, and dried *in vacuo*. The *product* was obtained as a very light brown powder which absorbed traces of water from the atmosphere. It decomposed, without melting, above 100° [Found: Pt, 61·8; C, 11·7; H, 2·0; Cl, 23·0; C_3H_6, liberated by aq. KCN, 13·4(5). $C_3H_6Cl_2Pt$ requires C_3H_6, 13·6%].

*Dipyridine*cyclo*propanedichloroplatinum.* "AnalaR" pyridine was condensed on to the first powder *in vacuo*, and the whole warmed to room temperature. No gas was evolved, but a white solid was formed, which dissolved in excess of pyridine to give a brown solution. Water was added and the *complex* was precipitated. It was filtered off, washed with water, and dried *in vacuo* (Found: Pt, 40·4; C, 33·6; H, 3·50; Cl, 15·0; C_3H_6, released by aq. KCN, 9·2. $C_{13}H_{16}N_2Cl_2Pt$ requires Pt, 41·9; C, 33·5; H, 3·44; Cl, 15·2; C_3H_6, 9·0%).

The infrared spectra were measured with a Grubb-Parsons double beam spectrometer. The finely powdered solid was suspended in hexachlorobutadiene for the region 2·5—4 μ and in "Nujol" for the region 4—14 μ.

The author thanks Dr. F. Glockling for helpful discussion.

DEPARTMENT OF INORGANIC AND PHYSICAL CHEMISTRY,
UNIVERSITY OF LIVERPOOL. [*Received, January 6th*, 1955.]

* The author thanks a referee for this suggestion.

Organosilicon Compounds. Part XIII. Co-ordination to Silicon.*

By C. Eaborn.

[Reprint Order No. 6017.]

With bases silicon tetrafluoride forms complexes in which silicon is 5- or 6-co-ordinated (Wilkins and Grant, *J.*, 1953, 927; Schumb and Cook, *J. Amer. Chem. Soc.*, 1953, **75**, 5133; Piper and Rochow, *ibid.*, 1954, **76**, 4318) but it has not been proved that co-ordination to silicon is involved in the complexes formed by chloro- and bromo-silanes (cf., *e.g.*, Harding, *J.*, 1887, **51**, 40; Trost, *Canad. J. Chem.*, 1951, **29**, 877, 1079; 1952, **30**, 835, 842; Burg, *J. Amer. Chem. Soc.*, 1954, **76**, 2674). Some, or all, of the complexes with amines may be quaternary ammonium salts, possibly solvated (cf. Emeléus and Miller, *J.*, 1939, 819; Piper and Rochow, *loc. cit.*), and co-ordination to halogen is as likely an explanation of the formation of 1 : 4 complexes between tetrachlorosilane and amines (Trost, *loc. cit.*) or tetrabromosilane and dioxan (Kennard and McCusker, *J. Amer. Chem. Soc.*, 1948, **70**, 1039) as Trost's suggestion that 4*s*, 3*d*, and 4*p* orbitals of silicon are involved in the co-ordination without disturbance of the sp^3 character of the Si–halogen bonds. There is no evidence that co-ordination to silicon occurs in silane derivatives other than halides, but it is often suggested as an initial rapid reaction step (*e.g.*, Gilman, Brook, and Miller, *ibid.*, 1953, **75**, 4531; Hauser and Hance, *ibid.*, 1951, **73**, 5846; Rochow, "The Chemistry of the Silicones," J. Wiley and Sons, New York, 2nd Edn. 1951, pp. 21—24), and Sujishi and Witz (*J. Amer. Chem. Soc.*, 1954, **76**, 4631) have attributed association in silyldimethylamine to intermolecular N→Si co-ordination. There is evidence against the existence of N→Si and O→Si co-ordination in organosilicon compounds, based on the strengths of organosilyl-alkylamines and carboxylic acids (Sommer and Rockett, *ibid.*, 1951, **73**, 5130), but in the aqueous media employed hydrogen-bonding to nitrogen and oxygen may break the co-ordination bonds.

We have now examined the ultraviolet absorption spectra of *p*-toluidine and pyridine in several organosilicon solvents. These conditions, in which fairly strong, relatively sterically-unhindered bases are dissolved in a large excess of the organosilanes, should favour N→Si co-ordination, and the consequent restriction on the lone pair of nitrogen should cause a large decrease in the absorption for *p*-toluidine and a marked increase in that for pyridine (cf. the effects of acids on the absorptions: Wohl, *Bull. Soc. chim. France*, 1939, **6**, 1312; Kumler and Strait, *J. Amer. Chem. Soc.*, 1943, **65**, 2349; Swain, Eisner, Woodward, and Brice, *ibid.*, 1949, **71**, 1341; Herington, *Discuss. Faraday Soc.*, 1950, **9**, 26). In no case, however, does the absorption differ significantly from that in *n*-hexane, suggesting that co-ordination to silicon is not such a ready process as is often assumed; *e.g.*, it seems unlikely that such co-ordination causes association in silyldimethylamine. The existence of such co-ordination in short-lived reaction intermediates is not, of course, ruled out, but should not be accepted until there is experimental evidence in its favour (cf. Eaborn and Parker, *J.*, 1955, 126).

	p-Toluidine				Pyridine		
Solvent.	$\lambda_{max.}$ (mμ)		$\lambda_{min.}$ (mμ)		$\lambda_{max.}$ (mμ)		$\lambda_{min.}$ (mμ)
n-Hexane...	293(1900)	237·5(9640)	267(580)	216(~350)	255·5(2010)	250·5(2080)	215(~220)
$SiMe_2Et_2$ ...	293(1960)	237·5(9260)	267·5(550)	—[a]	not studied		
$SiEt_3F$	293(2070)	—[a]	—[a]	—[a]	255·5(1970)	—[a]	—[a]
$C_6H_{11}·SiH_3$	294(1820)	238(9050)	268(570)	216(~350)	256(2020)	251(2090)	216(~200)
$Si(OEt)_4$ ...	296(2070)	240(10,000)	268(600)	217(~350)	255·5(1960)	250·5(2090)	216(~250)
$(SiMe_3)_2O$...	293(1810)	238(9250)	267·5(550)	215(~350)	255·5(1940)	250·5(2030)	215(~250)

[a] Low transmittance of solvent prevented measurement.

The Table lists the extinction coefficients (in parentheses) at the main maxima and minima.

Experimental.—cyclo*Hexylsilane*. This, b. p. 118°, n_D^{25} 1·4471 (Found: C, 63·6; H, 12·6. Calc. for $C_6H_{14}Si$: C, 63·1; H, 12·4%), was prepared in 90% yield from trichloro*cyclo*hexylsilane

* Part XII, *J.*, 1955, 1420.

and lithium aluminium hydride; Benkeser, Landesman, and Foster's directions for phenylsilane (*J. Amer. Chem. Soc.*, **1952**, **74**, 648) were followed except that the reaction mixture was boiled under reflux for 1 hr.

Spectra. A Unicam S.P.500 spectrophotometer was used. Emphasis was on relative rather than absolute accuracy in measurements of absorption intensities. The absorptions of the solutions did not change during some hours except for *p*-toluidine in tetraethoxysilane and triethylfluorosilane; for these the absorption increased, slowly in the former and more rapidly in the latter, with appearance of absorption at longer wavelengths. In the latter case the process was speeded by light and the solution became yellow. The reactions occurring were clearly not salt formation, which would lead to decrease in absorption, and they may have involved impurities in the solvent. The figures in the Table are for freshly prepared solutions.

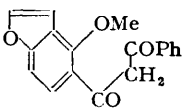
UNIVERSITY COLLEGE, LEICESTER. [*Received, January 7th*, 1955.]

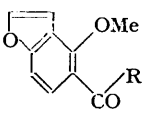
Chemistry of Pongamol. Part III. Synthesis.*

By S. K. MUKERJEE and T. R. SESHADRI.

[Reprint Order No. 6030.]

OF the possible methods for synthesis of pongamol (I) (Part II *), the condensation of 4-methoxybenzofuran-5-carbonyl chloride (II) with ethyl benzoylacetate in the presence of sodium ethoxide and of 5-acetyl-4-methoxybenzofuran (III) with ethyl benzoate did not proceed satisfactorily, but the simpler method in which the methyl ester (IV) was condensed with acetophenone proved convenient. The resulting pongamol (I) is best isolated and purified as the copper complex which is easily decomposed to yield pongamol. The synthetic and the natural product agree in melting point (mixed melting point), colour reaction with ferric chloride, and melting point of the copper complex, but differ in that

(I) 



(II; R = Cl)
(III; R = Me)
(IV; R = OMe)

in concentrated sulphuric acid the synthetic substance gives a permanent yellow colour whereas the natural sample, as originally recorded, yields a yellow colour becoming bright emerald-green in a few minutes. This seems to be due to an impurity in the natural product which is difficult to remove except by conversion into and decomposition of the copper complex. Pongamol recently obtained from *Tephrosia lanceolata* Grah. does not give the green colour with concentrated sulphuric acid but otherwise has all the properties of the sample obtained from *Pongamia glabra* (Rangaswami and Sastry, *Current Sci.*, **1955**, **24**, 13).

Experimental.—Methyl 4-methoxybenzofuran-5-carboxylate (Seshadri and Venkateswarlu, *Proc. Indian Acad. Sci.*, **1941**, **13**, *A*, 404) was prepared by refluxing a solution of the acid (1 g.) in dry acetone (50 c.c.) with methyl iodide (2 c.c.) and potassium hydrogen carbonate (5 g.) for 10 hr. It was obtained as a pale brown liquid and after being washed with aqueous sodium hydrogen carbonate and with water and dried was directly used for the next step.

The ester and acetophenone (1 c.c.) in dry ether (50 c.c.) were added to powdered sodamide (1 g.) covered with a layer of dry ether. The mixture was refluxed for 4 hr., left overnight, and then poured into excess of ice-cold dilute acetic acid, a brown semisolid mass separating. This was extracted with ether (6 × 25 c.c.), and the extract was repeatedly washed with aqueous sodium hydrogen carbonate (5%) and once with water. The bicarbonate extract on acidification yielded 4-methoxybenzofuran-5-carboxylic acid (0·4 g.), m. p. and mixed m. p. 148°. The ether solution was then concentrated to about 50 c.c. and vigorously shaken with saturated aqueous copper acetate. The ethereal layer became green and a yellowish-green crystalline precipitate gradually separated at the interface. After 24 hr. the precipitated complex was filtered off and washed first with a little ether and then with water. When dry, it crystallised

* Part II, *J.*, 1954, 1871.

from chloroform–ether as green rhombohedral tablets and prisms, m. p. 220—222° undepressed on admixture with the copper complex of natural pongamol.

The copper complex was suspended in 75% alcohol containing a little hydrochloric acid and warmed till a clear faintly greenish-yellow solution was obtained. Passage of hydrogen sulphide and filtration removed copper sulphide. The filtrate on concentration and cooling deposited pongamol as a brownish-yellow solid (0·2 g.). It crystallised from alcohol as pale brown rectangular tablets, melting alone or when mixed with the natural sample (from *P. glabra*) at 128—129°. It gave a blood-red colour with alcoholic ferric chloride and a yellow solution in concentrated sulphuric acid (Found : C, 73·5; H, 4·6. $C_{18}H_{14}O_4$ requires C, 73·5; H, 4·8%).

DEPARTMENT OF CHEMISTRY,
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p-*Nitrosoaniline.*

By J. WILLENZ.

[Reprint Order No. 6067.]

p-NITROSOANILINE was prepared by Fischer and Hepp (*Ber.*, 1887, **20**, 2474; see also Fischer and Schäffer, *Annalen*, 1895, **286**, 151) by heating " 1 part of *p*-nitrosophenol with 5 parts of ammonium chloride, 10 parts of dry ammonium acetate and a little ammonium carbonate." Fischer (*Ber.*, 1888, **21**, 684) claimed a 50% yield. Attempts to repeat this preparation using pure reactants in glass apparatus were unsuccessful, but reaction in an iron crucible in the presence of ferric chloride as catalyst gave *p*-nitrosoaniline in up to 34% yield.

Experimental.—A finely ground mixture of *p*-nitrosophenol (16·25 g.), ammonium chloride (81·25 g.), ammonium acetate (162·5 g.), ammonium carbonate (17·5 g.), and ferric chloride (1·75 g.) was heated in an iron crucible on a steam-bath for 45 min. after which the mixture was homogeneous. The liquid product was poured into water at 0° to precipitate the crude *p*-nitrosoaniline. Dissolution in dilute sulphuric acid, filtration, basification with ammonia, and recrystallisation from benzene gave *p*-nitrosoaniline as bluish-black needles, (5·5 g., 34%), m. p. 173—174° (lit., 173—174°). The *monopicrate*, purified by precipitation from methanol with chloroform, decomposed at 166° (Found : C, 40·8; H, 2·8; N, 19·7. $C_{12}H_9O_8N_5$ requires C, 41·0; H, 2·6; N, 19·9%). The addition *compound* with 2 : 4-dinitrophenol had m. p. 116—117° (olive green crystals from ethanol) (Found : C, 46·7; H, 3·4; N, 18·2. $C_{12}H_{10}O_6N_4$ requires C, 47·0; H, 3·3; N, 18·3%).

RESEARCH DEPARTMENT, IMPERIAL CHEMICAL INDUSTRIES LIMITED,
BILLINGHAM DIVISION, BILLINGHAM, CO. DURHAM. [*Received, January 25th*, 1955.]

The Alkaloids of Picralima nitida, *Stapf, Th. and H. Durand. Part III.* A Note on Akuammicine and* pseudo*Akuammicine.*

By SIR ROBERT ROBINSON and A. F. THOMAS.

[Reprint Order No. 6087.]

THE separation of the petroleum-soluble bases of *Picralima* seeds has been described in Part II.* By means of its sparingly soluble hydrochloride (cf. Henry, *J.*, 1932, 2759), *pseudo*akuammicine is readily purified.

The formula, $C_{19}H_{20}O_2N_2$, proposed by Henry (*loc. cit.*) for akuammicine should now be replaced by $C_{20}H_{22}O_2N_2$ whereas *pseudo*akuammicine appears to be $C_{19}H_{20}O_2N_2$. The latter base has been available in very small amount; its infra-red absorption spectrum overlies that of akuammicine.

The ultra-violet spectra of akuammicine and echitamidine are characteristic and almost identical (Raymond-Hamet, *Compt. rend.*, 1951, **233**, 560); tabernosine (Janot, Goutarel,

* Part II, *J.*, 1954, 352.

and Le Men, *Bull. Soc. chim. France*, 1954, 707) and *pseudo*-akuammicine are from this point of view further members of the group. The indication is that the peculiar structure of the bands is due to an indole nucleus with additional conjugation. This is doubtless associated with the abnormally high rotatory powers of the bases, with the curious and possibly significant exception that *pseudo*akuammicine has a rotatory power within the more usual range.

The deep absorption band at 6·03 μ exhibited by akuammicine and *pseudo*akuammicine (Millson, Robinson, and Thomas, *Experientia*, 1953, **9**, 89) was naturally interpreted as due to an amide-carbonyl group but if this is correct the group is quite stable towards lithium aluminium hydride. Further experiment is needed to resolve this apparent contradiction.

Added in Proof.—Under more vigorous conditions this reduction has now been effected by K. Aghoramurthy (personal communication).

Experimental.—Akuammicine hydrochloride crystallised slowly from water or aqueous alcohol as large glistening plates which on drying in a vacuum-desiccator broke into small leaflets, m. p. 143—146°. The leaflets contained $4H_2O$, half of which was removed on drying at 120°/0·01 mm. for 4 hr. The *dihydrate* had m. p. 171°, $[\alpha]_D^{21}$ −610° (*c*, 1·430 in EtOH) (Found: C, 61·0; H, 6·6; N, 7·1; Cl, 9·1. $C_{20}H_{22}O_2N_2,HCl,2H_2O$ requires C, 60·9; H, 6·9; N, 7·1; Cl, 8·8%).

The *base* crystallised from ethanol and a little water in colourless plates, m. p. 182°, $[\alpha]_D^{16}$ −745° (*c*, 0·994 in EtOH), pK_a 7·45 (Found: C, 74·6, 74·8; H, 7·1, 7·2; N, 8·6, 8·9. $C_{20}H_{22}O_2N_2$ requires C, 74·5; H, 6·9; N, 8·7%). The *perchlorate* separated from aqueous ethanol in lustrous needles of the dihydrate, m. p. 134—136° (Found: loss, 4·3. Found, in the dried sample: C, 55·0; H, 5·7; N, 6·9; Cl, 8·4. $C_{20}H_{22}O_2N_2,HClO_4,H_2O$ requires C, 54·5; H, 5·6; N, 6·4; Cl, 8·0%). The *hydriodide*, made from the hydrochloride and concentrated potassium iodide solution, crystallised from water in colourless, square plates of the dihydrate, m. p. 128° (Found: loss, 3·8. Found, in dried material: C, 51·4; H, 5·4; N, 6·0; I, 27·1. $C_{20}H_{22}O_2N_2,HI,H_2O$ requires C, 51·3; H, 5·4; N, 6·0; I, 27·1%).

Akuammicine develops a fine royal blue colour when a trace of dichromate is added to its solution in 80% sulphuric acid but it gives no characteristic reaction with ferric chloride in weak acid solution. It gives a bright green solution in concentrated nitric acid. The base does not couple with diazobenzenesulphonic acid under any conditions tried but, after reduction in boiling acetic acid with zinc dust and a trace of mercuric chloride, the product is convertible into a typical methyl-orange showing the usual indicator changes. This is probably due to a reduction either of an amide group (or C:N) or of an aromatic indole nucleus.

A solution of akuammicine in dilute acid becomes bright yellow on the addition of sodium nitrite.

The base was recovered unchanged after attempted reduction with lithium aluminium hydride in ether (2 hr.) or tetrahydrofuran (5 hr.). It was also stable to boiling methanolic potassium hydroxide (3%; 1½ hr.) and to boiling N-hydrochloric acid (2 hr.).

An attempt to acetylate the base was made as follows: akuammicine (200 mg.) was dissolved in dry pyridine (5 c.c.) and acetic anhydride (0·4 c.c.). Next day the mixture was diluted with water, and solid potassium hydrogen carbonate added. A precipitate was slowly formed, which had m. p. 178°, but on recrystallisation proved to be unchanged akuammicine. pseudo-*Akuammicine hydrochloride* crystallised from water as the monohydrate which can be completely dried only with great difficulty. After 5 hr. at 120°/0·01 mm. it had m. p. 217° (decomp. to red froth), $[\alpha]_D^{18}$ approx. 0 (*c*, 0·7 in 50% EtOH) [Found: loss 3·1. Found, in dried material: C, 64·8; H, 6·5; N, 8·3; Cl, 10·5, *C*-Me, 4·0. $C_{19}H_{20}O_2N_2$ (+2% of H_2O) requires C, 64·9; H, 6·3; N, 8·0; Cl, 10·1; *C*-Me, 4·3%].

The *base* forms glistening plates with a bluish lustre, m. p. 187° (decomp. to red froth), after recrystallisation from aqueous ethanol, $[\alpha]_D^{19}$ −83°, pK_a 7·47 (Found: C, 73·9; H, 6·6; N, 9·2. $C_{19}H_{20}O_2N_2$ requires C, 74·1; H, 6·6; N, 9·1%). The *perchlorate* separates as glistening needles from water or as leaflets from ethanol; it is very sparingly soluble in all solvents used, but with a 3-dm. tube, $[\alpha]_D^{21}$ approx. 0 (*c*, 0·2 in EtOH) was observed (Found: C, 55·7; H, 5·7; N, 6·6; Cl, 8·4. $C_{19}H_{20}O_2N_2,HClO_4,\frac{1}{2}C_2H_5{\cdot}OH$ requires C, 55·6; H, 5·6; N, 6·5; Cl, 8·2%).

The colour reactions of *pseudo*akuammicine are similar to those of akuammicine.

DYSON PERRINS LABORATORY, OXFORD. [*Received, February 1st*, 1955.]

The Resolution of 3-*Methylpent*-1-*yn*-3-*ol.*

By J. R. HICKMAN and J. KENYON.

[Reprint Order No. 6097.]

THE resolution of tertiary alcohols into their optical antipodes has presented considerable difficulty and it is only fairly recently (Doering and Zeiss, *J. Amer. Chem. Soc.*, 1950, **72**, 147; Zeiss, *J. Amer. Chem. Soc.*, 1951, **73**, 2391) that the practicability of such resolutions has become generally accepted. We now describe the preparation of optically active (+)-3-methylpent-1-yn-3-ol, CH:C·CMeEt·OH.

The alcohol was converted into its hydrogen phthalate, whose brucine salt was fractionally crystallised from acetone. The (+)-(hydrogen phthalate) was obtained from the brucine salt in the usual manner (see Table 1). From this ester was obtained the (+)-alcohol (see Table 2).

The present alcohol is the first tertiary acetylenic alcohol to be resolved and apparently presents the simplest and most straightforward resolution of any tertiary alcohol.

TABLE 1. *Specific rotatory powers of* (+)-1-*ethyl*-1-*methylprop*-2-*ynyl hydrogen phthalate in various solvents at room temperature* (*c*, 5·000).

Solvent	Temp.	$[\alpha]_{4358}$	$[\alpha]_{4800}$	$[\alpha]_{5086}$	$[\alpha]_{5461}$	$[\alpha]_{5780}$	$[\alpha]_{5893}$	$[\alpha]_{4358}/[\alpha]_{5461}$
Ethanol	19°	+95·6°	+64·8°	+58·8°	+48·0°	+44·0°	+39·0°	1·99
Ether	20	77·2	53·2	46·6	38·6	32·0	30·6	2·00
Acetone	18	72·6	49·6	45·8	36·4	32·8	29·2	2·00
Pyridine	19	64·2	47·2	40·4	33·0	28·0	27·0	1·95
Chloroform ...	18	60·4	41·2	39·6	30·0	27·2	24·2	2·01
Benzene	18	54·2	36·4	35·4	25·8	24·4	22·8	2·10

TABLE 2. *Observed rotatory powers of* (+)-3-*methylpent*-1-*yn*-3-*ol at* 21° (*l*, 1).

α_{4358}	α_{4800}	α_{5086}	α_{5461}	α_{5780}	α_{5893}	α_{6438}
+4·36°	+3·34°	+3·10°	+2·58°	+2·26°	+2·22°	+1·50°

(−)-1-Ethyl-1-methylprop-2-ynyl hydrogen phthalate was prepared by fractional crystallisation of partially lævorotatory hydrogen phthalate obtained from mixed intermediates of the corresponding brucine salt; the highest specific rotation obtained was $[\alpha]_{5893}^{18}$ −22·3° (*c*, 6·16 in benzene).

Experimental.—(±)-3-*Methylpent*-1-*yn*-3-*ol.* The alcohol was obtained by treating ethyl methyl ketone with ethynylmagnesium halide by the Grignard method, and had b. p. 121—122°/760 mm., m. p. 30—31°, n_D^{20} 1·4318, d_{20}^{20} 0·8721 (Found: C, 74·0; H, 10·3. Calc. for $C_6H_{10}O$: C, 73·5; H, 10·2%).

The alcohol (41 g.), phthalic anhydride (65 g.), and pyridine (65 g.) were heated at 90° for 2 hr., then treated with dilute hydrochloric acid and extracted with ether. The ether extract was washed with dilute hydrochloric acid, then with water, and dried. The crude hydrogen phthalate, after removal of the ether, was purified by dissolution in sodium carbonate solution and extraction with ether to remove unchanged alcohol; the aqueous solution was then acidified with dilute hydrochloric acid, and extracted with chloroform, and the extract dried. After removal of the chloroform, the inactive *hydrogen phthalate* (47 g., 45·5%) was obtained in cubes, m. p. 97—98° (Found, by titration with KOH: *M*, 244. $C_{14}H_{14}O_4$ requires *M*, 246).

Use of triethylamine in place of pyridine gave an 81% yield of much darker product.

(+)-1-*Ethyl*-1-*methylprop*-2-*ynyl hydrogen phthalate.* (±)-3-Methylpent-1-yn-3-yl hydrogen phthalate (47 g.) and anhydrous brucine (77 g.) were dissolved in the minimum quantity of boiling acetone and allowed to cool. Fine needles separated slowly, attaining optical purity after a total of six crystallisations. The final brucine salt had m. p. 148—149°. This was decomposed with dilute hydrochloric acid and extracted with ether, the extract washed and dried, and the ether removed, giving (+)-1-*ethyl*-1-*methylprop*-2-*ynyl hydrogen phthalate*, m. p. 112—113° (Found: *M*, 245).

(−)-1-*Ethyl*-1-*methylprop*-2-*ynyl hydrogen phthalate.* A mixture of the more soluble fractions produced in the resolution was decomposed into the partially pure lævorotatory hydrogen phthalate by means of dilute hydrochloric acid followed by ether-extraction and recovery of the ether

after washing and drying the extract. This material, $[\alpha]_{5893}^{20}$ −14·2° (*c*, 5·00; l, 1), was recrystallised four times from light petroleum and then had $[\alpha]_{5893}^{18}$ −22·3° (*c*, 5·00; l, 1), m. p. 112—113° (Found: *M*, 245).

(+)-3-*Methylpent*-1-*yn*-3-*ol*. The (+)-ester (18 g.) was steam-distilled with a slight excess of 10N-potassium hydroxide; the (+)-alcohol was then extracted from the distillate with ether, and the extract dried and fractionated. (+)-3-*Methylpent*-1-*yn*-3-*ol* (5 g.) thus obtained had b. p. 120—121°/760 mm., n_D^{19} 1·4317 (Found: C, 73·8; H, 10·5. $C_6H_{10}O$ requires C, 73·5; H, 10·2%).

(±)-1-*Ethyl*-1-*methylprop*-2-*ynyl* p-*nitrobenzoate*. The (±)-alcohol (1·0 g.), *p*-nitrobenzoyl chloride (2·0 g.), and pyridine (5·0 g.) at 90° rapidly gave this *ester*, plates (2·4 g.) (from aqueous alcohol), m. p. 68—69° (Found: C, 63·5; H, 5·4; N, 6·6. $C_{13}H_{13}O_4N$ requires C, 63·2; H, 5·3; N, 5·7%).

The (+)-*ester*, similarly prepared, had m. p. 75—76°, $[\alpha]_{5893}^{20}$ +12·8° (*l*, 0·5; *c*, 1·72 in EtOH).

(±)-1-*Ethyl*-1-*methylprop*-2-*ynyl hydrogen phthalate from its optical antipodes*. 0·200 g. each of pure (+)- and (−)-1-ethyl-1-methylprop-2-ynyl hydrogen phthalate were ground together and then had m. p. 97—99° and $[\alpha]_{5893}^{20}$ 0·00° (*l*, 0·5; *c*, 5·00 in C_6H_6).

Reduction of partially active (−)-3-*methylpent*-1-*yn*-3-*ol to the corresponding fully saturated inactive alcohol*. Partially lævorotatory 3-methylpent-1-yn-3-ol (3 g.) was reduced in ether solution with hydrogen (Pd–C) yielding 3-methylpentan-3-ol (2·2 g.), b. p. 122—123°, n_D^{20} 1·4183, d_4^{20} 0·8235 and having zero optical rotation.

BATTERSEA POLYTECHNIC, LONDON, S.W.11. [*Received, February 3rd*, 1955.]

2-*Alkoxypropenes*.

By H. P. CROCKER and R. H. HALL.

[Reprint Order No. 6114.]

DURING a recent study of the infrared absorption spectra of various αβ-unsaturated ethers (Philpotts and Ward, unpublished work), certain 2-alkoxypropenes were required. Some of these had been prepared previously (cf. Claisen, *Ber.*, 1898, **31**, 1019; Schmitt and Boord, *J. Amer. Chem. Soc.*, 1932, **54**, 751; Sherrill and Walter, *ibid.*, 1936, **58**, 743; Dolliver, Gresham, Kistiakowsky, Smith, and Vaughan, *ibid.*, 1938, **60**, 440; Shostakovskiĭ and Gracheva, *J. Gen. Chem. U.S.S.R.*, 1953, **23**, 1153); in the present instance they were conveniently obtained from the corresponding 2 : 2-dialkoxypropanes (cf. Claisen, *loc. cit.*). The physical constants of the methoxy- and *n*-propoxy-propene thus prepared, however, differed considerably from those recorded recently by Shostakovskiĭ and Gracheva (*loc. cit.*) and proof of structures was therefore required. Infrared absorption data showed that the unsaturated ethers were all very similar and elementary analyses, hydrogenation of the ethoxypropene to ethyl *iso*propyl ether, identical with an authentic specimen, and ozonolysis of the *iso*butoxypropene to formaldehyde and *iso*butyl acetate established that they were correctly formulated as 2-alkoxypropenes. Shostakovskiĭ and Gracheva's data (*loc. cit.*) may possibly refer to materials contaminated with alcohol: careful purification was necessary to afford spectroscopically pure specimens, free from the alcohol liberated in their preparation.

The 2 : 2-dialkoxypropanes required were accessible from acetone, either directly by reaction with orthoformic esters (cf. Claisen, *Ber.*, 1898, **31**, 1010) or by way of *iso*propenyl acetate (cf. Croxall, Glavis, and Neher, *J. Amer. Chem. Soc.*, 1948, **70**, 2805). The latter route was the one employed.

Experimental.—2 : 2-*Dialkoxypropanes*. These were prepared from *iso*propenyl acetate by the method of Croxall, Glavis, and Neher (*loc. cit.*), with the exception that yellow mercuric oxide was substituted for the red oxide. The yields and physical constants of the products are shown in Table 1. 2 : 2-*Di*-n-*propoxy*- and 2 : 2-*di*iso*butoxy*-*propane* are new compounds.

2-*Alkoxypropenes*. The following general method was used (cf. Claisen, 1898, **31**, 1019). The 2 : 2-dialkoxypropane (1 mol.) was added to a slurry of phosphoric oxide (1·1 mol.) and quinoline (1·1 mol.) (phosphoric oxide alone, or phosphoric acid, was unsatisfactory), and the mixture was heated in an oil-bath (140—180°) under a helices-packed column (2 × 30 cm.), fitted with a

TABLE 1. 2 : 2-*Dialkoxypropanes*, $Me_2C(OR)_2$.

R	Yield (%)	B. p.	n_D^{20}	R	Yield (%)	B. p.	n_D^{20}
Me	33	81°/756 mm.[a]	1·3778[a]	*n*-Pr[c]	44	91°/95 mm.	1·4026
Et	52[b]	113°/754 mm.[b]	1·3886[b]	*iso*-Bu[d] ...	32	65°/14 mm.	1·4068

[a] Claisen (*Ber.*, 1898, **31**, 1010) gives b. p. 83°; Killian, Hennion, and Nieuwland (*J. Amer. Chem. Soc.*, 1934, **56**, 1384) give b. p. 78—80°/747 mm., n_D^{20} 1·3746. [b] Croxall *et al.* (*ibid.*, 1948, **70**, 2805) give a yield of 55%, b. p. 113—113·5°, n_D^{20} 1·3891. [c] Found: C, 67·45; H, 12·7. $C_6H_{12}O_2$ requires C, 67·45; H, 12·6%. [d] Found: C, 70·55; H, 12·7. $C_{11}H_{24}O_2$ requires C, 70·15; H, 12·85%.

variable take-off still-head. Crude product was taken off at the lowest head-temperature attainable. 2 : 2-Di*iso*butoxypropane was readily de-alcoholated; the dimethoxy-compound required more prolonged heating (36 hr.). The yield of crude product was about 10% in excess of theory.

In the case of 2-ethoxypropene the infrared spectrum of the crude product showed that about 20% of ethyl alcohol was present. This could not be removed completely by fractionation, as an azeotrope, b. p. 58°/747 mm., n_D^{20} 1·3871, containing 10% of alcohol, was formed.

The crude ethers were purified by repeated washing with successive small amounts of water, dried (KOH), and fractionated from unchanged ketal. With the more water-soluble methyl ether flakes of sodium were added and when no more effervescence occurred the liquid was fractionated.

The yields and properties of the ethers are summarised in Table 2. 2-iso*Butoxypropene* is a new compound.

TABLE 2. 2-*Alkoxypropenes*, $CH_2{:}CMe{\cdot}OR$.

R	Yield (%)[a]	B. p.	n_D^{20}	Formula	Found (%) C	Found (%) H	Calc. (%) C	Calc. (%) H
Me	22	33·5°/750 mm.[b]	1·3827[b]	C_4H_8O	66·4[c]	11·5[c]	66·65	11·2
Et	26	61°/747 mm.[d]	1·3918[d]	$C_5H_{10}O$	69·75	11·4	69·75	11·7
n-Pr	44	88·5°/756 mm.[e]	1·4017[e]	$C_6H_{12}O$	72·0	12·1	72·0	12·1
iso-Bu	53	104·5°/752 mm.	1·4043	$C_7H_{14}O$	74·15	12·2	73·65	12·35

[a] Spectroscopically and analytically pure material. [b] Shostakovskii and Gracheva (*J. Gen. Chem. U.S.S.R.*, 1953, **23**, 1153) give b. p. 28°/759 mm., n_D^{20} 1·3751; Claisen (*Ber.*, 1898, **31**, 1019) gives b. p. 38°. [c] Analysis difficult owing to volatile nature of compound; figures quoted are mean of five determinations. Shostakovskii and Gracheva (*loc. cit.*) analysed a polymer of the ether. [d] *Idem* (*loc. cit.*) give b. p. 63—64°/749 mm., n_D^{20} 1·3913; Sherrill and Walter (*J. Amer. Chem. Soc.*, 1936, **58**, 743) give b. p. 61·2—61·8°/760 mm., n_D^{20} 1·3913; Schmitt and Boord (*ibid.*, 1952, **54**, 751) give b. p. 61—63°/748 mm. n_D^{20} 1·3915; Dolliver *et al.* (*ibid.*, 1938, **60**, 440) give b. p. 61·90°/765 mm., n_D^{20} 1·3927. [e] Shostakovskii and Gracheva (*loc. cit.*) give b. p. 78·5°/756 mm., n_D^{20} 1·3990.

Hydrogenation of 2-ethoxypropene. The ether (7·65 g.) in toluene (50 ml.) was shaken in hydrogen in the presence of Adams catalyst (0·1 g.) (1·15 mol. of hydrogen absorbed). Infrared examination of the crude product (5·2 g.), b. p. 53—54°/752 mm., n_D^{20} 1·3632—1·3702, recovered from the solvent by fractionation, showed that it consisted of ethyl *iso*propyl ether, together with traces of compounds containing hydroxyl and carbonyl groups. It was therefore washed with water (5 × 10 ml.), dried (Na), and distilled, giving a product, n_D^{20} 1·3638, the infrared spectrum of which was virtually indistinguishable from that of a synthetic sample of ethyl *iso*propyl ether of b. p. 54·5°/756 mm., n_D^{20} 1·3632 (cf. Bennett and Philip, *J.*, 1928, 1931).

Ozonolysis of 2-iso*butoxypropene.* Ozonised oxygen was passed at room temperature through a solution of the ether (15 g.) in carbon tetrachloride (250 ml.) until the exit gases contained ozone. The solution was concentrated under reduced pressure and the ice-cold residue was agitated with a stream of nitrogen whilst a slurry of zinc dust (20 g.) in water (80 ml.) was added. The resultant mixture was kept overnight at room temperature and the zinc dust then filtered off and washed with ether. The aqueous filtrate, after extraction with ether (4 × 20 ml.), yielded the dimedone derivative of formaldehyde, m. p. and mixed m. p. 189°. The combined ether washings and extracts were dried (Na_2SO_4) and evaporated to give *iso*butyl acetate (7·5 g.) (Found: equiv., 115. Calc. for $C_6H_{12}O_2$: equiv., 116), from which *p*-bromophenacyl acetate, m. p. and mixed m. p. 85°, was prepared.

The authors thank Mr. T. E. Couling for assistance with the experimental work and Mr. A. R. Philpotts and Mr. W. R. Ward for infrared absorption data. They are also indebted to Dr. R. N. Lacey for a generous sample of *iso*propenyl acetate and to the Directors of the Distillers Company, Ltd., for permission to publish this note.

THE DISTILLERS CO., LTD., RESEARCH AND DEVELOPMENT DEPT.,
GREAT BURGH, EPSOM, SURREY.

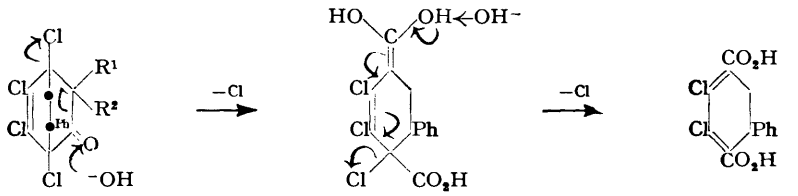
[*Received, February 9th*, 1955.]

Hydration of a Bridged α-Diketone.

By R. H. BURNELL and W. I. TAYLOR.

[Reprint Order No. 6123.]

PREVIOUSLY we postulated (*J.*, 1954, 3636) that the base-catalysed rearrangement of 1 : 2 : 3 : 4-tetrachloro-5 : 6-dioxo-7-phenyl*bicyclo*[2 : 2 : 2]oct-2-ene (I) proceeded *via* a keten intermediate to give the dicarboxylic acid (IV). Although the substance (I) has an absorption maximum (λ **446** mμ, ε 175) typical of an α-diketone (cf. Leonard and Mader, *J. Amer. Chem. Soc.*, 1950, **72**, 5388) in dry benzene, yet in aqueous or aqueous-ethanolic solution this band was replaced by a maximum at 310 mμ (ε 174) indicative of an isolated ketone group (cf. Cookson, *J.*, 1954, 282). This is best interpreted as due to hydration of one of



(I) $R^1R^2 = O$
(II) $R^1 = R^2 = OH$

(III)

(IV)

the keto-groups to form the structure (II); hence the monohydrate isolated by Horner and Merz (*Annalen*, 1950, **570**, 89) is a true compound. The rearrangement of the compound (I) in alkaline solution therefore takes place according to the annexed scheme, where the intermediate (III) satisfactorily replaces the high-energy keten proposed earlier. Thus the first step in this reaction is a special case of base-catalysed fission of the type:

$$R^1{\cdot}CO{\cdot}CR^2R^3{\cdot}CR^4R^5X + OH^- \longrightarrow R^1{\cdot}CO_2H + CR^2R^3{:}CR^4R^5 + X^-$$

For a summary of examples of this reaction see Eschenmoser and Frey (*Helv. Chim. Acta*, 1952, **35**, 1660).

The carbonyl stretching frequencies of the diketone (I) at 1770 and 1750 cm.$^{-1}$ and of the " hydrate " (II) at 1770 cm.$^{-1}$ are very high and are thought to be a measure of the rigidity of the system and the effect of the carbon–chlorine dipoles on the neighbouring carbonyl groups. Although it is well known that 1 : 2 : 3-triketones are easily hydrated, α-diketones, *e.g.*, camphorquinone, $\lambda_{max.}$ 474 mμ (ε 38·4 in 95% ethanol; ε 36·1 in light petroleum), do not become hydrated. In our case there must be an increase in stability of the molecule through hydration or, in other words, some relief in the steric strain in going from structure (I) to structure (II).

The infrared spectra were measured in potassium bromide discs by Mr. W. Fulmor and staff, American Cyanamid Co., Lederle Laboratories Division. We are indebted to the National Research Council of Canada for a grant.

UNIVERSITY OF NEW BRUNSWICK, CANADA. [*Received, February 11th*, 1955.]

α- *and* β-*Methyl* L-*Fucofuranosides.*

By WINIFRED M. WATKINS.

[Reprint Order No. 6155.]

FOR studies on the enzymic degradation of the blood-group mucoids, the methyl L-fucosides were required as possible synthetic substrates. α- and β-Methyl L-fucopyranosides have been obtained crystalline (Hockett, Phelps, and Hudson, *J. Amer. Chem. Soc.*, 1939, **61**, 1658) but the furanosides have not been described. Augestad, Berner, and Weigner (*Chem. and Ind.*, 1953, 376) and Augestad and Berner (*Acta Chem.*

Scand., 1954, **8**, 251) reported the preparation of new crystalline methylfuranosides of galactose, arabinose, and xylose and the separation of the isomeric glycosides on a column of powdered cellulose. They found that a boiling methanolic solution containing very little hydrogen chloride gave the best yield of the furanosides and this method has now been employed in the preparation of the methyl L-fucofuranosides. By separation on a cellulose column α-methyl L-fucofuranoside was isolated in a crystalline form and β-methyl L-fucofuranoside as a syrup.

Experimental.—L-Fucose (1 g.) was heated in methanol (50 ml.) containing 0·012% of hydrogen chloride under reflux until it no longer reduced Fehling's solution (6 hr.). Hydrogen chloride was removed with lead carbonate, and the solution evaporated to a syrup which was examined by paper chromatography with ethyl methyl ketone saturated with water as solvent. The papers were sprayed with sodium metaperiodate followed by Schiff's decolorised magenta reagent (Buchanan, Dekker, and Long, *J.*, 1950, 3162), and the syrup was shown to contain four substances all of which were faster-running than L-fucose. One had an R_F value identical with that of α-methyl L-fucopyranoside (Fischer, *Ber.*, 1895, **28**, 1160); these spots were greenish-purple in colour. Two of the components, which ran more quickly than the α-pyranoside and by analogy with the methyl galactosides described by Augestad and Berner (*loc. cit.*) were thought to be the α- and β-furanoside, gave bright blue spots with Schiff's spray. The fourth spot, which moved more slowly than the α-pyranoside, gave a purplish-blue spot.

A concentrated solution of the syrup in ethyl methyl ketone was placed at the top of a column (50 × 2 cm.) of powdered cellulose. Ethyl methyl ketone saturated with water was used as the mobile phase and the effluent, collected automatically in 3-ml. fractions, left the column at the rate of 36 ml. per hour. One drop of each fraction was placed on filter paper and sprayed with periodate and Schiff's reagent. The spots developed a blue colour at tube no. 35 and a colour was detected continuously up to tube no. 150. The fractions were pooled in pairs, dried (Na_2SO_4), and examined in the polarimeter. The material eluted first (fractions 34—54) showed a positive rotation and the values obtained gave a symmetrical peak. The succeeding fractions gave a negative rotation but did not show a well-defined peak. Chromatograms were then run on the contents of every other tube and it was found that tube nos. 35—48 contained a single component and that the second-fastest-running component was present alone in tubes 55—64. The intermediate tubes contained a mixture of the two materials. Fractions 75—78 gave crystalline α-methyl L-fucopyranoside, m. p. 153°, $[\alpha]_D$ −196° (*c*, 1% in H_2O), and fractions 120—150 crystalline β-methyl L-fucopyranoside, m. p. 121°, $[\alpha]_D$ +10° (*c*, 1% in H_2O).

β-Methyl L-fucofuranoside. Fractions 35—48 were pooled and evaporated to a syrup which was redissolved in dry ethyl acetate, heated with charcoal, filtered, and concentrated. The clear syrup obtained had $[\alpha]_D$ +113 (*c*, 2% in H_2O). A paper chromatogram showed that only one sugar derivative was present, and hydrolysis with N-hydrochloric acid for 24 hr. at 100° followed by estimation of reducing sugar by Nelson's method (*J. Biol. Chem.*, 1944, **153**, 375) indicated that the syrup was 99% methyl glycoside. The syrup has not crystallised, however, after six months at −18°. A 0·2% solution of the material was 50% hydrolysed in 100 hr. by N-hydrochloric acid at room temperature. β-Methyl L-fucopyranoside was not detectably hydrolysed under the same conditions.

Crystalline α-methyl L-fucofuranoside. Fractions 55—64 were pooled and on evaporation the syrup crystallised spontaneously. Chromatographic examination showed that only one sugar derivative was present. A 0·2% solution of the material in N-hydrochloric acid was 50% hydrolysed after 24 hr. at room temperature, whereas a 0·2% solution of α-methyl L-fucopyranoside in the same acid did not become reducing after 128 hr. at room temperature. After recrystallisation from dry ethyl acetate the *α-methyl L-fucofuranoside* had m. p. 125—126°, $[\alpha]_D$ −108° (*c*, 2% in H_2O) (Found: C, 47·4; H, 8·1; OMe, 17·6. $C_7H_{14}O_5$ requires C, 47·2; H, 7·9; OMe, 17·4%).

This work was carried out during the tenure of a Beit Memorial Research fellowship.

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A Wolff–Kishner Reduction Procedure for Sterically Hindered Carbonyl Groups.

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[Reprint Order No. 6166.]

The reduction of sterically hindered carbonyl groups by either the Clemmensen or the Wolff–Kishner procedure is not easily effected. In his classical work on adrenocortical steroids Reichstein (see Steiger and Reichstein, *Helv. Chim. Acta*, 1938, **21**, 161) removed the very hindered ketone group of an 11-oxo-steroid using modified Clemmensen conditions (heavily amalgamated zinc). An alternative Wolff–Kishner procedure for the reduction of 11-oxo-steroids was reported by Moffett and Hunter (*J. Amer. Chem. Soc.*, 1951, **73**, 1973). This employs sodium methoxide in methanol at 200° with "anhydrous" hydrazine. Neither of these methods of reduction is suited for relatively large-scale work. We have found that, whilst the Wolff–Kishner procedure of Huang-Minlon (*ibid.*, 1949, **71**, 3301), as indeed he states, does not reduce sterically hindered carbonyl groups, the simple precaution of using *completely* anhydrous hydrazine and keeping all water, so far as possible, out of the reaction system improves its reducing power remarkably. This reduction procedure was first developed by us for the preparation of fairly large quantities of lanostanol from 7 : 11-dioxolanostanyl acetate (see Barton, Ives, and Thomas, *J.*, 1954, 903). It has been used successfully in the reduction of 11-oxo-steroids (Djerassi and Thomas, *Chem. and Ind.*, 1954, 1228) and of hindered triterpenoid ketones (Beaton, Spring, Stevenson, and Stewart, *ibid.*, 1955, **35**; personal communication from Professor Carl Djerassi). Its application in the reduction of certain hindered 15-oxo-steroids has also been mentioned (Woodward, Patchett, Barton, Ives, and Kelly, *J. Amer. Chem. Soc.*, 1954, **76**, 2852; *Chem. and Ind.*, 1954, 605).

Experimental.—Reduction of 7 : 11-*dioxolanostanyl acetate.* Sodium (10 g.) in diethylene glycol (500 ml.; redistilled) was heated to 180° (all temperatures measured with thermometer in liquid) and *completely anhydrous* hydrazine [prepared by refluxing hydrazine hydrate (60 ml.; 100%) over sodium hydroxide pellets (60 g.) for 3 hr.] was distilled in until the mixture refluxed freely at 180°. All operations were carried out in all-glass apparatus carefully protected from atmospheric moisture. The solution was cooled, 7 : 11-dioxolanostanyl acetate (Dorée, McGhie, and Kurzer, *J.*, 1948, 988) (50 g.) added quickly, and the solution refluxed overnight. The temperature was then raised to 210° by distilling some of the hydrazine back into the hydrazine generator and the solution refluxed at this temperature for 24 hr. Dilution with water and benzene-extraction gave, after reacetylation in the usual way and crystallisation from chloroform–methanol, lanostanyl acetate (Voser, Mantavon, Günthard, Jeger, and Ruzicka, *Helv. Chim. Acta*, 1950, **33**, 1893; McGhie, Pradhan, Cavalla, and Knight, *Chem. and Ind.*, 1951, 1165) (32 g., 69%), m. p. 149—150°, resolidifies and remelts at 156—157°, $[\alpha]_D$ +40° (*c*, 1·67 in $CHCl_3$).

Two of us (D. A. J. I. and B. R. T.) are indebted to the International Wool Secretariat for (respectively) Predoctorate and Postdoctorate Research Fellowships.

Birkbeck College, London, W.C.1. [*Received, February 22nd*, 1955.]