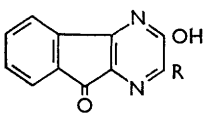
NOTES.

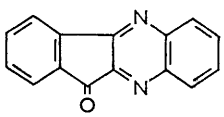
681. *The Formation of Yellow Condensation Products from Amino-compounds and Ninhydrin.*

By A. W. JOHNSON and D. J. MCCALDIN.

IN a previous paper [1] we have discussed the structure of the well-known yellow condensation product of proline and ninhydrin. Other amino-compounds outside of the proline group produce yellow spots on paper chromatograms after development with ninhydrin. Some of these condensations have now been examined and it is found that, unlike proline, there is present in most of these amino-compounds a suitably placed methylene group or another amino-group which is capable of further condensation with the 1-oxo-group of ninhydrin to produce a new five- or six-membered ring. This reaction takes precedence over the normal Strecker degradation of the amine or amino-acid that leads to formation of the purple ninhydrin condensation product. An example of an amino-acid derivative yielding a yellow ninhydrin condensation product is glycine amide which reacts to form the polycyclic compound (I; R = H) or a tautomer. Under similar conditions, alanine amide gives (I; R = Me). Spectral evidence favours the tautomeric structure (I). The ultraviolet absorption shows a bathochromic shift after addition of alkali in common with the behaviour of 3-hydroxypyridine,[2] 3-hydroxyquinoline,[3] and 2-hydroxy-3-methylquinoxaline,[4] and unlike 2-pyridone [2] and 2-quinolone.[3] Moreover, the infrared absorption of compound (I; R = Me) showed a strong band at 1725 cm.$^{-1}$ (cyclopentanone carbonyl).



(I)



(II)

Yellow colours with ninhydrin have been reported [5] from the substituted glycine amides, *N*-glycylglucosamine and *N*-glycyl-α-ribofuranosylamine. The condensation product (II) from ninhydrin and *o*-phenylenediamine, described many years ago by Ruhemann,[6] is an example of a related condensation.

Activation of a methylene or methene group in the amino-compound can be achieved by its proximity to an oxo-group or by its position in a suitable heterocyclic ring. Although the pure condensation products have not been isolated, examples of this type of amino-compound reported to give yellow ninhydrin colours include aminoacetone,[7]

[1] Johnson and McCaldin, *J.*, 1958, 817.
[2] Specker and Gawrosch, *Ber.*, 1942, **75**, 1338.
[3] Ewing and Steck, *J. Amer. Chem. Soc.*, 1946, **68**, 2181.
[4] Lanning and Cohen, *J. Biol. Chem.*, 1951, **189**, 109.
[5] Baddiley, Buchanan, Prescott, *et al.*, *J.*, 1956, 2818; 1957, 4769.
[6] Ruhemann, *J.*, 1910, **97**, 1449.
[7] Ellis, Petrow, and Snook, *J. Pharm. Pharmacol.*, 1949, **1**, 60; 1950, **2**, 128, 535; Elliott, *Biochim. Biophys. Acta*, 1958, **29**, 446.

2-amino-5-methyl-4-oxohexanoic acid,[8] 2-aminomethylbenzimidazole,[9] pyridoxamine,[10] and β-indolylglycine.[11]

Experimental.—Condensation of ninhydrin and glycine amide. Glycine amide [12] (66 mg.) was dissolved in the minimum amount of methanol, and methanolic ninhydrin hydrate (132 mg.) was added. The mixture became dark yellow after a few minutes and was shaken at room temperature for 16 hr. The yellow crystals (46 mg.) of the condensation product (I; R = H) were separated and washed with ether and ethanol. After crystallisation from ethanol the *product* formed brownish yellow elongated prisms which discoloured above 275° and had m. p. 321—323° (decomp.) (Found: C, 66·9; H, 3·0; N, 14·2. $C_{11}H_6N_2O_2$ requires C, 66·6; H, 3·15; N, 14·1%). Light absorption: (i) in methanol, $\lambda_{max.}$ 236, 264, 301, 310, 356, and 371 mμ; log ε 4·44, 4·04, 4·11, 4·11, 4·00, and 3·95, respectively; (ii) in methanol containing N/100-sodium hydroxide solution, $\lambda_{max.}$ 240, 285, 301, 310, 367, and 428 mμ; log ε 4·81, 4·13, 4·12, 4·28, 3·98, and 3·56, respectively.

Condensation of ninhydrin and alanine amide. Alanine amide (66 mg.) and ninhydrin hydrate (120 mg.) reacted as described above to give the *product* (I; R = Me) as yellow elongated prisms (47 mg.) which were washed with a little methanol and dried. After crystallisation from methanol it had m. p. 324—325° (Found: C, 67·7; H, 3·6; N, 13·0. $C_{12}H_8N_2O_2$ requires C, 67·9; H, 3·6; N, 13·2%). Light absorption: (i) in methanol, $\lambda_{max.}$ 222, 278, 285, 324, and 334 mμ; log ε 4·39, 4·02, 4·13, 3·98, and 3·92, respectively; (ii) in methanol containing N/100-sodium hydroxide solution, $\lambda_{max.}$ 239, 300, 311, 356, and 367 mμ; log ε 4·51, 4·25, 4·37, 4·07, and 4·06, respectively.

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[*Received, October 22nd*, 1959.]

[8] Ellington, Hassall, Plimmer, and Seaforth, *J.*, 1959, 80.
[9] Crawford and Edward, *J.*, 1956, 673.
[10] Kalyankar and Snell, *Nature*, 1957, **180**, 1069.
[11] J. B. Jepson, private communication.
[12] Yang and Rising, *J. Amer. Chem. Soc.*, 1931, **53**, 3183.

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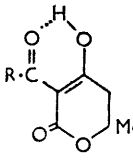
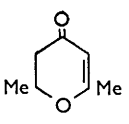
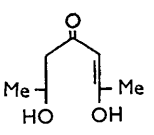
682. *Alternaric Acid. Part IV.* 3-Acetyl-5,6-dihydro-4-hydroxy-6-methyl-2-pyrone.*

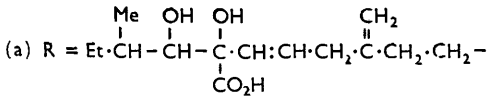
By J. R. BARTELS-KEITH and W. B. TURNER.

THE nature of the chromophore of alternaric acid (Ia) [1] has been confirmed by comparison of its properties with those of the simpler pyrone (Ib), prepared by hydrogenation of dehydroacetic acid over palladised charcoal.


(I)


(IIa)


(IIb)


(a) R = Et·CH(Me)–CH(OH)–C(OH)(CO$_2$H)·CH:CH·CH$_2$·C(=CH$_2$)·CH$_2$·CH$_2$–

(b) R = Me

The ultraviolet absorption (Table) of the dihydropyrone (Ib) agrees well with that obtained by subtraction of the end absorption of the acid [2] R·CO$_2$H from the absorption

* Part III, *J.*, 1960, 1662.

[1] Bartels-Keith and Grove, *Proc. Chem. Soc.*, 1959, 398.
[2] Bartels-Keith, *J.*, 1960, 860.

of alternaric acid. In 0·1N-sodium hydroxide the ultraviolet absorption spectra of alternaric acid (Ia) and the dihydropyrone (Ib) are virtually identical.

Ultraviolet absorption spectra: $\lambda_{max.}$ (mμ) *and* ε (*in parentheses*).

In EtOH	(Ib)	216 (9,500)	271 (10,630)
,,	(Ia) — $R{\cdot}CO_2H$	216 (8,570)	275 (11,300)
In 0·1N-NaOH	(Ib)	249 (16,000)	268 (13,500)
,,	(Ia) [3]	250 (15,000)	271 (14,000)

The infrared spectra of the pyrone (Ib) and methyl alternarate are very similar in the 1550—1750 $cm.^{-1}$ region. The former shows bands (in $CHCl_3$) at 1711, 1638, and 1560 (broad) $cm.^{-1}$, and the latter at 1710, 1643, and 1560 (broad) $cm.^{-1}$ (in addition to that at 1726 $cm.^{-1}$ due to the methoxycarbonyl group).

The thermodynamic pK values (4·62 and 4·67 respectively) at 25° of the ester and dihydropyrone (Ib) show good agreement.

Both compounds (Ia) [3,4] and (Ib) with N-sulphuric acid yield 1 mol. of carbon dioxide and with N-sodium hydroxide yield acetone and acetaldehyde.

Acid-hydrolysis of compound (Ib) by boiling N-sulphuric acid or, better, by 90% sulphuric acid at 130°, gives, in addition to carbon dioxide, a liquid, $C_7H_{10}O_2$, whose spectroscopic properties suggested its formulation as (IIa). This compound has recently been obtained [5] by hydrogenation of 2,6-dimethyl-4-pyrone and its properties agree with those of ours. Its formation from the dihydropyrone (Ib) is analogous to that of 2,6-dimethyl-4-pyrone from dehydroacetic acid. The compound (IIa) gives an intense reddish-violet colour with ferric chloride and shows a bathochromic shift in 0·1N-sodium hydroxide, indicating that in aqueous solution it exists in the open-chain form (IIb).

Experimental.—*3-Acetyl-5,6-dihydro-4-hydroxy-6-methyl-2-pyrone* (Ib). Dehydroacetic acid (5·0 g.) in methanol (250 ml.) was hydrogenated over 10% palladium–charcoal (2·1 g.) until the ultraviolet absorption showed that most of the starting material had been reduced (E_{273}/E_{305} = 2·35; uptake 1·1 mols.). The product, isolated in the usual way, was distributed in a counter-current apparatus containing the system ether–buffer (citric acid–phosphate; pH 5). After 60 transfers, measurement of the ultraviolet absorption of the ethereal layers showed that tubes 30—47 contained material with $\lambda_{max.}$ 273 mμ while tubes 55—60 contained starting material; the intermediate tubes contained mixtures.

The contents of tubes 30—47 were combined and the ethereal layer was separated, dried, and evaporated to small volume; needles of m. p. 98—99° (893 mg.) separated. Further concentration of the mother-liquor yielded a second crop, m. p. 90—98° (417 mg.).

The aqueous layer from tubes 30—47 was acidified and extracted continuously with ether for 24 hr. Concentration of the dried ethereal solution gave needles, m. p. 97—98° (651 mg.).

Pure *2-acetyl-5,6-dihydro-4-hydroxy-6-methyl-2-pyrone* (Ib), m. p. 98—100°, was obtained by recrystallisation from methanol followed by sublimation at 85°/10 mm. (Found: C, 56·9; H, 6·0. $C_8H_{10}O_4$ requires C, 56·5; H, 5·9%). It gives the following colour reactions (cf. alternaric acid [3]): orange with ferric chloride; wine-red with titanous chloride; transient blue with titanous chloride–pyridine.

In a second experiment complete separation of the product (Ib) was obtained by 90 transfers.

Acid hydrolysis of the dihydropyrone (Ib). (*a*) The compound (168·5 mg.) was heated under reflux with N-sulphuric acid (20 ml.) in a stream of nitrogen, the issuing gases passing through 0·1N-barium hydroxide, 1·03 mols. of carbon dioxide were evolved in 4 hr.

In a separate experiment, with 133 mg., the mixture was extracted with methylene chloride,

[3] Grove, *J.*, 1952, 4056.
[4] Bartels-Keith, *J.*, 1960, 1662.
[5] de Vrieze, *Rec. Trav. chim.*, 1959, **78**, 91.

and the solvent was evaporated through a Vigreux column, leaving a residue which on distillation gave fractions (i) b. p. 70° (bath)/10 mm., showing strong OH absorption (3450 $cm.^{-1}$) and a single carbonyl band (1710 $cm.^{-1}$), and (ii) b. p. up to 120° (bath)/10 mm., with infrared spectrum identical with that of 2,3-dihydro-2,6-dimethyl-4-pyrone (IIa) (see below).

(*b*) A mixture of the dihydropyrone (Ib) (1·05 g.) and 90% sulphuric acid (2·3 ml.) was heated at 120—130° until effervescence had almost subsided (*ca.* ½ hr.), cooled, and poured into ice-water. The product, isolated with methylene chloride, distilled as a yellow oil, b. p. 100° (bath)/10 mm. Two further distillations gave pure 2,3-dihydro-2,6-dimethyl-4-pyrone (IIa), $n_D^{23.5}$ 1·4908 (Found: C, 66·4; H, 8·0. Calc. for $C_7H_{10}O_2$: C, 66·6; H, 8·0%), $\lambda_{max.}$ (in EtOH) 263 mμ (ε 10,500) (in 0·1N-NaOH) 298 mμ (ε 11,000), $\nu_{max.}$ 3464wk, 1665, and 1608 $cm.^{-1}$, giving a reddish-violet colour with ferric chloride [*semicarbazone*, plates, m. p. 177—178° (Found: C, 52·0; H, 7·3. $C_8H_{13}O_2N_3$ requires C, 52·4; H, 7·15%); 2,4-dinitrophenylhydrazone, m. p. 151—153° (de Vrieze [5] gives b. p. 85—86°/14 mm.), n_D^{26} 1·4952, $\lambda_{max.}$ 263 mμ (ε 6900); 2,4-dinitrophenylhydrazone, m. p. 152°, for 2,3-dihydro-2,6-dimethyl-4-pyrone].

Alkaline hydrolysis. The dihydropyrone (Ib) (174 mg.), treated with N-sodium hydroxide under the conditions used for alternaric acid,[4] yielded acetaldehyde dimethone, m. p. and mixed m. p. 140—141°, and acetone 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 125—126°.

We are indebted to Mr. B. D. Akehurst for technical assistance.

IMPERIAL CHEMICAL INDUSTRIES LIMITED, AKERS RESEARCH LABORATORIES,
THE FRYTHE, WELWYN, HERTS. [*Received, January 29th*, 1960.]

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683. *The Preparation of Iodosilanes from Phenylchlorosilanes.*

By B. J. AYLETT and I. A. ELLIS.

SILYL IODIDE and silylene iodide were first prepared by Emeléus, Maddock, and Reid,[1] using the controlled iodination of silane with hydrogen iodide. The direct reaction of silane and iodine at low temperature also yields these compounds.[2] Any method involving silane, however, is somewhat hazardous, and an alternative was sought by which quantities of the order of 10 g. of each iodosilane could be made, free from the other members of the series.

The chlorination of phenyltrichlorosilane [3] yielded mainly chlorophenyltrichlorosilane; this compound was then reduced with lithium aluminium hydride in diethyl ether to give chlorophenylsilane. Hydrogen iodide reacted with chlorophenylsilane in a sealed tube at room temperature to give mainly chlorobenzene and silyl iodide; no silylene iodide was detected in the products. The last stage is similar to one mentioned without details by Mayo *et al.*,[4] in which silyl bromide was prepared by the reaction of phenylsilane with hydrogen bromide. However, phenylsilane and hydrogen iodide would yield an inseparable mixture of silyl iodide and benzene, and the initial chlorination was needed to avoid this. Some hydrogen was evolved, and this, together with analytical evidence, suggests that the involatile residue after fractionation contained a little chlorophenyliodosilane.

Diphenylsilane similarly reacted with hydrogen iodide to give a mixture of silylene iodide, benzene, and traces of hydrogen, silyl iodide, and silicoiodoform. Disproportion is thus perceptible in this case, probably as a result of weak complex formation between

[1] Emeléus, Maddock, and Reid, *J.*, 1941, 353.
[2] Sujishi, personal communication.
[3] Yakubovitch and Motsarev, *Zhur. obshchei Khim.*, 1956, **26**, 568; *Doklady Akad. Nauk S.S.S.R.*, 1953, **91**, 277.
[4] Mayo, Opitz, and Peake, *J. Chem. Phys.*, 1955, **23**, 1344.

benzene and silylene iodide; evidence that weak donors have this effect on halogenosilanes has recently been reviewed.[5] Chlorobenzene is a very weak donor, and does not appear to cause disproportionation of silyl iodide.

Experimental.—Preparation of silyl iodide. Phenyltrichlorosilane (25 g.) was purified by fractional condensation at −46° *in vacuo* and chlorinated by Yakubovitch and Motsarev's method.[3] To the yellowish liquid product was added anhydrous ether (25 ml.); the whole was slowly added to a mixture of lithium aluminium hydride (16 g.) and ether (30 ml.) contained in a nitrogen-filled three-necked flask fitted with a reflux condenser and guard tube. Reaction was very vigorous; after being kept overnight the contents of the flask were nearly solid. All volatile products were removed by pumping (6 hr.) and warming of the flask, and after repeated fractionation *in vacuo* yielded a fraction held at −64° [Found: *M* (vapour), 142 ± 1. Calc. for $Cl{\cdot}C_6H_4{\cdot}SiH_3$: *M*, 142·7], together with silane (0·070 g.) (Found: *M*, 33. Calc. for SiH_4: *M*, 32·1), ether, chlorobenzene (0·3 g.) (Found: *M*, 112 ± 1. Calc. for C_6H_5Cl: *M*, 112·6), and a liquid (2 g.) of low volatility that on hydrolysis yielded hydrogen and dichlorobenzene (possibly $Cl_2C_6H_3{\cdot}SiH_3$).

The fraction corresponding to chlorophenylsilane was placed in a thick-walled Pyrex tube (~100 ml.) in a dry-box, and anhydrous hydrogen iodide (25 g.) distilled in. After being sealed, the tube was allowed to warm slowly to room temperature; a clear pale red liquid was formed, which evolved gas slightly. After 12 hr., there was no change in colour, but gas evolution had stopped. The volatile products were removed and fractionated *in vacuo*, yielding: hydrogen (30 ml. at N.T.P.), excess of hydrogen iodide, silyl iodide (11 g.; 60%) (Found: *M*, 158. Calc. for SiH_3I: *M*, 157·9. V. p. 12·3 cm./0°; m. p. −56° ± 2; lit.,[1] 12·39 cm./0° and −57°), chlorobenzene (v. p. 7 mm./16°; lit.,[6] 7·1 mm./16°), and a liquid held at −23° which on alkaline hydrolysis yielded hydrogen, iodide ion, and chlorobenzene (possibly $ClC_6H_4{\cdot}SiH_2I$). An involatile yellow-green liquid (0·1 ml.) left in the tube was almost all soluble in benzene, but gave a little hydrogen on hydrolysis.

Preparation of silylene iodide. Diphenylsilane (20 g.), prepared from diphenyldichlorosilane by reduction with lithium aluminium hydride,[7] was allowed to react with excess of hydrogen iodide as described above. After fractionation, the products were: a trace of silane, excess of hydrogen iodide, a mixed fraction A (*M*, 81·0), benzene, silylene iodide (17 g.; 55%) (Found: H, 0·7; I, 89·1%; *M*, 279 ± 5. Calc. for SiH_2I_2: H, 0·7; I, 89·4%; *M*, 284. V. p. 3·8 mm./0°; lit., 4·2 mm./0°), and an involatile liquid (0·2 ml.) that gave hydrogen, silicate, and iodide ion on alkaline hydrolysis (Found: H : I, 1 : 2·88. Calc. for $SiHI_3$: 1 : 3·00). The benzene [8] and silylene iodide [9] had infrared spectra identical with those of the pure materials, and fraction A had a spectrum corresponding to a mixture of benzene and silyl iodide.[10] The fraction was treated with a little water, yielding disilyl ether (infrared spectrum [11]), and then dried (CaH_2) and refractionated. The product (Found: *M*, 78·3. Calc. for C_6H_6: *M*, 78·1) consisted only of benzene.

UNIVERSITY OF ABERDEEN, OLD ABERDEEN, SCOTLAND. [*Received, February 4th*, 1960.]

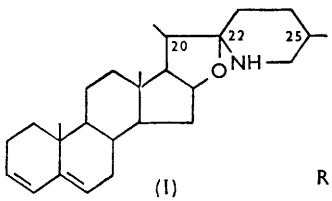
[5] Aylett, *J. Inorg. Nuclear Chem.*, in the press.
[6] Dreisbach and Martin, *Ind. Eng. Chem.*, 1949, **41**, 2875.
[7] Benkeser, Landesman, and Foster, *J. Amer. Chem. Soc.*, 1952, **74**, 648.
[8] Pierson, Fletcher, and Gantz, *Analyt. Chem.*, 1956, **28**, 1218.
[9] Emeléus, MacDiarmid, and Maddock, *J. Inorg. Nuclear Chem.*, 1955, **1**, 194.
[10] Dixon and Sheppard, *Trans. Faraday Soc.*, 1957, **53**, 282.
[11] Lord, Robinson, and Schumb, *J. Amer. Chem. Soc.*, 1956, **78**, 1327.

684. Solanum *Alkaloids. Part XIV.* The* NH *Stretching Intensities of Solasodine, Tomatidine, and Some Derivatives.*

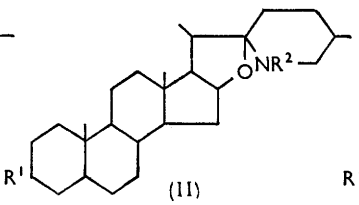
By L. H. Briggs, L. D. Colebrook, H. K. Miller, and Y. Sato.

In our studies on *Solanum* alkaloids we have found that the NH stretching band of the secondary amino-group cannot be detected in the infrared spectra of these compounds under normal conditions: it appears only when exceptional concentrations or cell lengths are used.

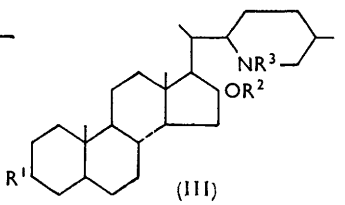
Bellamy [1] lists the NH stretching vibration of secondary amines as a single band of medium intensity at 3500—3300 cm.$^{-1}$. Jones and Sandorfy [2] list the range 3500—3400 cm.$^{-1}$ for the free NH stretching band of secondary amines. Marion, Ramsay, and Jones [3] give a range, 3480—3440 cm.$^{-1}$, for the same group, but they note that while



(I)



(II)



(III)

the band persists in piperidine and related structures with much reduced intensity in some cases it cannot be detected in chloroform solution. Our present results are in agreement.

It was first observed that solaso-3,5-diene (I; 20α, 22*a*, 25D) (Nujol mull; sodium chloride prism) failed to absorb in this region. "α"-Solasodan (II; $R^1 = R^2 = H$; 5α, 20α, 22*a*, 25D), "β"-solasodan (II; $R^1 = R^2 = H$; 5β, 20α, 22*a*, 25D), and solaso-3,5-diene, lacking hydroxyl groups which, in some circumstances, could possibly mask NH absorption, were then examined in potassium bromide discs in the range 5000—2600 cm.$^{-1}$, with a lithium fluoride prism in a Beckman IR-2 spectrophotometer. "α"-Solasodan and solaso-3,5-diene were also examined in carbon tetrachloride solution. Concentrations were selected so that the intensity of the CH stretching absorption was about 95%. Under these conditions no NH absorption was observed. However, saturated solutions of "α"-solasodan and solaso-3,5-diene in carbon tetrachloride in a 1·05 mm. cell exhibited definite but weak NH stretching bands at 3360 and 3351 cm.$^{-1}$ respectively.

Solasodine (II; Δ^5; R^1 = β-OH, $R^2 = H$; 20α, 22*a*, 25D), tomatidine (II; R^1 = β-OH, $R^2 = H$; 5α, 20α, 22*a*, 25L), and some of their derivatives, however, required a cell length of 20 mm. owing to their low solubility in carbon tetrachloride and carbon disulphide. A Beckmann IR-7 prism-grating instrument was used for this section of the work. Under these conditions compounds with a free NH group show a sharp but weak band at 3373—3334 cm.$^{-1}$ (see Table). For comparison, piperidine and morpholine are included in the Table.

* Part XIII, *J.*, 1958, 1422.

[1] Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 2nd edn., pp. 251—252.

[2] Jones and Sandorfy, in "Technique of Organic Chemistry," ed. Weissberger, Interscience Publ., Inc., New York, 1956, Vol. IX, p. 511.

[3] Marion, Ramsay, and Jones, *J. Amer. Chem. Soc.*, 1951, **73**, 305.

Compound	Solvent	NH stretch (cm.$^{-1}$)	Compound	Solvent	NH stretch (cm.$^{-1}$)
Piperidine [a]	CCl_4	3343	Solaso-3,5-diene	CCl_4	3351
,, ...	$CHCl_3$ [c]	3334	Tomatidine	CS_2	3336
Morpholine	$CHCl_3$ [c]	3338	Dihydrotomatidine [b]	CCl_4	3373
Solasodine	CS_2	3348			

[a] When kept, solutions of piperidine in carbon tetrachloride become cloudy through the formation of piperidine hydrochloride. [b] Dihydrotomatidine (III; R^1 = β-OH, $R^2 = R^3$ = H; 5α, 20α, 22*a*, 25L). [c] 0·12 mm. cell.

An indication that this absorption is indeed attributable to the NH stretching vibration follows from a consideration of compounds belonging to the solasodine and tomatidine series in which the amine-hydrogen atom has been replaced, *e.g.*, *N*-methyltomatidine (II; R^1 = β-OH, R^2 = Me; 5α, 20α, 22*a*, 25L), acetyl-*N*-methylsolasodine (II; Δ^5; R^1 = OAc, R^2 = Me; 20α, 22*a*, 25D), diacetylsolasodine (II; Δ^5; R^1 = OAc, R^2 = Ac; 20α, 22*a*, 25D), triacetyldihydrosolasodanol (III; R^1 = OAc, $R^2 = R^3$ = Ac; 5α, 20α, 22*a*, 25D), and 30,*N*-diacetyldihydrosolasodanol (III; R^1 = OAc, R^2 = H, R^3 = Ac; 5α, 20α, 22*a*, 25D). None of these compounds has any absorption in the 3373—3334 cm.$^{-1}$ region except the last, which shows a strong, bonded hydroxyl band at 3366 cm.$^{-1}$.

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685. *The Characterisation of α-Methyl-lævulic Acid.*

By R. Brettle.

α-Methyl-lævulic acid has been characterised in the past by several ketonic derivatives. Of these, the phenylhydrazone is unstable [1] and the D-(+)-tartramazone [2] relatively inaccessible, whilst the m. p. of the semicarbazone is recorded [1,3,4] variously as 177—178°, 182—183°, and 191—192°. Recent workers have characterised α-methyl-lævulic acid as the 2,4-dinitrophenylhydrazone.[2,5]

Although the acid with Brady's reagent [6] at 20° gave the 2,4-dinitrophenylhydrazone, a warm solution of 2,4-dinitrophenylhydrazine in ethanolic sulphuric acid readily converted α-methyl-lævulic acid into the ethyl ester 2,4-dinitrophenylhydrazone. Lævulic acid,[7] and some other keto-acids,[8] behave similarly. To avoid possible esterification, the 2,4-dinitrophenylhydrazone of α-methyl-lævulic acid was crystallised from nitroethane rather than from ethanol.

[1] Braude and Timmons, *J.*, 1953, 3313.
[2] Wiley, Gerzon, Flynn, Sigal, Weaver, Quarck, Chauvette, and Monahan, *J. Amer. Chem. Soc.*, 1957, **79**, 6062.
[3] Nazarov and Elizarova, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1951, 295.
[4] Behal, *Bull. Soc. chim. France*, 1901, **25**, 245.
[5] Djerassi, Halpern, Wilkinson, and Eisenbraun, *Tetrahedron*, 1958, **4**, 369.
[6] Brady, *J.*, 1931, 756.
[7] Strain, *J. Amer. Chem. Soc.*, 1935, **57**, 758.
[8] Cf. Cook and Linstead, *J.*, 1934, 946; Drayson, Lewis, and Polgar, *J.*, 1958, 430.

α-Methyl-lævulic acid has now also been characterised through the carboxyl function as the *p*-bromophenacyl ester and the *S*-benzylthiouronium salt.

Experimental.—Derivatives of α-methyl-lævulic acid. Ethyl 2-acetylbut-2-enoate, b. p. 105—110°/20 mm., was prepared in 44% yield by condensation of acetaldehyde and ethyl acetoacetate in the presence of piperidine at −10°. Knoevenagel [9] gives b. p. 107°/20 mm. α-Methyl-lævulic acid, b. p. 142—144°/16 mm., was prepared from the unsaturated ester by Huan's method [10] in 41% yield. Huan [10] gives b. p. 138—141°/11 mm. The 2,4-dinitrophenylhydrazone, prepared by adding a cold ethanolic solution of the acid to Brady's reagent [6] at 20°, was crystallised three times from nitroethane and then had m. p. 188—189° (Found: C, 46·3; H, 4·4; N, 17·9. Calc. for $C_{12}H_{14}O_6N_4$: C, 46·45; H, 4·5; N, 18·1%). Wiley and his co-workers [2] give m. p. 190—194°. Djerassi and his co-workers [5] give m. p. 191—192°. When α-methyl-lævulic acid was added to Brady's reagent [6] at 40° the product, obtained as orange needles by crystallisation from ethanol, was the *ethyl ester* 2,4-*dinitrophenylhydrazone*, m. p. 90° (Found: C, 49·8; H, 5·4; N, 16·7. $C_{14}H_{18}O_6N_4$ requires C, 49·7; H, 5·3; N, 16·6%). The p-*bromophenacyl ester* had m. p. 76° after crystallisation successively from ethanol and aqueous acetone (Found: C, 51·6; H, 4·4; Br, 24·4. $C_{14}H_{18}O_4Br$ requires C, 51·4; H, 4·6; Br, 24·4%). The S-*benzylthiouronium salt* had m. p. 124° after crystallisation from water (Found: C, 57·0; H, 6·8; N, 9·6; S, 11·0. $C_{14}H_{20}O_3N_2S$ requires C, 56·75; H, 6·8; N, 9·5; S, 10·8%).

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[9] Knoevenagel, *Ber.*, 1898, **31**, 730.
[10] Huan, *Bull. Soc. chim. France*, 1938, 1341.

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686. *Attempted Reduction of Rhodium Tetrafluoride and Platinum Tetrafluoride with Selenium Tetrafluoride.*

By M. L. HAIR and P. L. ROBINSON.

SELENIUM TETRAFLUORIDE has been used as a mild reducing agent for fluorides by Hepworth, Robinson, and Westland,[1] and its application by Bartlett and Hepworth [2] produced pure palladous fluoride. Attempts to reduce rhodium tetrafluoride and platinum tetrafluoride in a similar way led to the isolation of the complexes $(RhF_4)_2,SeF_4$, and $PtF_2,2SeF_4$. Although both these complexes underwent thermal decompositon, in neither instance was a lower fluoride isolated; the former gave a dark-coloured mixture of rhodium trifluoride and rhodium metal, the latter was reduced directly to metallic platinum.

Experimental.—Rhodium tetrafluoride was prepared by the action of bromine trifluoride on rhodium tribromide and, after the excess of bromine trifluoride had been removed, selenium tetrafluoride was condensed upon it. When refluxed at atmospheric pressure, the selenium tetrafluoride reacted with the rhodium tetrafluoride, without dissolving it, to give a pale pink solid. Analysis indicated the compound $(RhF_4)_2,SeF_4$; the colour is understandable since Sharpe's unstable RhF_4–BrF_3 complex was pink.[3]

The *complex* readily dissolved in aqueous sodium carbonate. The solution was divided into three portions: rhodium was determined as the metal by direct precipitation from the boiling solution with formic acid, selenium as the element by reduction with sulphur dioxide in hydrochloric acid solution, and fluorine as lead chlorofluoride [Found: Rh, 41·1; Se, 15·1; F, 44·9. $(RhF_4)_2,SeF_4$ requires Rh, 40·1; Se, 15·4; F, 44·5%].

[1] Hepworth, Robinson, and Westland, *Chem. and Ind.*, 1955, 1156.
[2] Bartlett and Hepworth, *Chem. and Ind.*, 1956, 1425.
[3] Sharpe, *J.*, 1950, 3444.

Platinum tetrafluoride was prepared from bromine trifluoride and platinous bromide after Sharpe's method.[3] Selenium tetrafluoride in an excess was condensed on to the pale brown platinic fluoride. Reaction was slow at room temperature but on warming proceeded more quickly, converting the platinic fluoride into a cream-coloured solid without its appearing to dissolve in the selenium tetrafluoride. Removal of the excess of reagent under reduced pressure left a solid, $PtF_2,2SeF_4$. On heating, this decomposed, leaving metallic platinum.

The *complex* fumed in moist air and was hydrolysed vigorously by water to a yellow solution from which, on acidification with hydrochloric acid, both platinum and selenium were precipitated, the former by zinc and the latter by sulphur dioxide. Acidification of the solution with sulphuric acid and distillation gave a distillate from which the fluorine was precipitated as lead chlorofluoride (Found: Pt, 34·9; Se, 28·4; F, 36·0. $PtSe_2F_{10}$ requires Pt, 35·9; Se, 29·1; F, 35·0%).

This work was carried out during the tenure of a Salters' Scholarship (M. L. H.).

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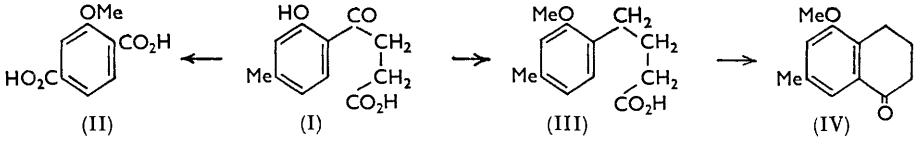
687. β-*Aroylpropionic Acids. Part XVII.* Establishment of the Structure of* β-(2-*Hydroxy*-p-*toluoyl*)*propionic Acid.*

By A. M. EL-ABBADY, F. G. BADDAR, and A. LABIB.

THE acid, m. p. 154°, obtained by Raval, Bokil, and Nargund [1] from succinic anhydride and *m*-cresol in presence of anhydrous aluminium chloride, was supposed by them to be β-(2-hydroxy-4-toluoyl)propionic acid (I) from the bluish-brown colour it gives with alcoholic ferric chloride; but, they did not rigidly establish its structure. The present investigation confirmed this structure by the following two routes; (i) Treatment with methyl sulphate gave the corresponding methoxy-ester whence alcoholic potassium hydroxide generated the methoxy-acid which was oxidised by alkaline potassium permanganate to methoxyterephthalic acid (II). (ii) The methoxy-acid from (I) was reduced by Clemmensen's method to γ-(2-methoxy-4-tolyl)butyric acid (III) which was cyclised to the tetralone (IV).



(II) (I) (III) (IV)

Experimental.—Methyl β-(2-*methoxy*-4-*toluoyl*) *propionate* (I). The acid [2] (5 g., 1 mol.) was boiled for 12 hr. with methyl sulphate (12 g.) and anhydrous potassium carbonate (30 g.) in acetone (15 ml.). The *product* (5·1 g., 83%), crystallised from benzene–light petroleum (b. p. 60—80°), had m. p. 65—66° (Found: C, 66·3; H, 7·0. $C_{13}H_{16}O_4$ requires C, 66·1; H, 6·8%).

The ester was boiled with 3% alcoholic potassium hydroxide for 2 hr. The *methoxy-acid* (4·4 g.), crystallised from benzene, had m. p. 127—128° (Found: C, 64·7; H, 6·0. $C_{12}H_{14}O_4$ requires C, 64·85; H, 6·35%).

Oxidation of β-(2-*methoxy*-4-*toluoyl*)*propionic acid.* β-(2-Methoxy-4-toluoyl)propionic acid

* Part XVI, *J.*, 1960, 2556.

[1] Raval, Bokil, and Nargund, *J. Univ. Bombay*, 1938, **7**, 184.
[2] Awad, Baddar, and Marei, *J.*, 1954, 4538.

(1 g.), 3% potassium hydroxide solution (40 ml.), and potassium permanganate (3 g.) were heated on a boiling-water bath for 1 hr. The manganese dioxide was dissolved by adding sodium hydrogen sulphite, and the solution was cooled in ice, then acidified with concentrated hydrochloric acid. The precipitated acid (0·6 g.), when crystallised from water, gave methoxyterephthalic acid (II), m. p. 286—288°, undepressed on admixture with an authentic specimen (lit.,[3] m. p. 277—279°) (Found: C, 55·0; H, 4·05. Calc. for $C_9H_8O_5$: C, 55·1; H, 4·1%).

γ-(2-Methoxy-4-tolyl)butyric Acid (III). The acid (I) (2 g.) was reduced by Martin's modified Clemmensen's method (30 hours' reflux). The precipitated acid (1·8 g.) was crystallised from light petroleum (b. p. below 40°) to give *γ-(2-methoxy-4-tolyl)butyric acid*, m. p. 54—55° (Found: C, 68·8; H, 7·9. $C_{12}H_{16}O_3$ requires C, 69·2; H, 7·7%).

5-Methoxy-7-methyl-1-tetralone (IV). The butyric acid (III) (1 g.) was refluxed with phosphorus oxychloride (0·5 ml.) in tetrachloroethane (10 ml.) for 2 hr. The mixture was hydrolysed with cold water, then steam-distilled. 5-Methoxy-7-methyl-1-tetralone was obtained as a light yellow oil, b. p. 150—152°/5 mm. It gave a *2,4-dinitrophenylhydrazone*, m. p. 223—224° (from acetic acid) (Found: C, 58·1; H, 4·8; N, 14·9; OMe, 8·0. $C_{18}H_{18}O_5N_4$ requires C, 58·4; H, 4·9; N, 15·1; OMe, 8·4%).

Microanalyses are by Dr. A. Bernhardt, Max-Plank-Institut, Mulheim (Ruhr).

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[3] Schall, *Ber.*, 1879, **12**, 828.

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688. *An Improved Synthesis of Phenyl α-D-Galactopyranoside.*

By M. J. CLANCY.

PHENYL α-D-GALACTOPYRANOSIDE is an important substrate in the study of galactosidases [1] and a convenient preparation of this compound in good yield is here described. The galactoside has been obtained in low yield by de-*O*-acetylating the product of the reaction between tetra-*O*-acetyl-α-D-galactopyranosyl bromide and phenol catalysed by quinoline.[2] It has also been synthesised by condensing phenol with penta-*O*-acetyl-β-D-galactose [3] or penta-*O*-acetyl-α-D-galactose,[4] with zinc chloride as catalyst in both cases. The product is then de-*O*-acetylated. The use of penta-*O*-acetyl-α-D-galactose introduces an additional stage since this compound is prepared from its β-anomer.[5] The yields obtained in these preparations were not recorded, but Professor Courtois informs us that an overall yield of 15% is usual in the case of the preparation *via* the α-anomer.

Penta-*O*-acetyl-β-D-galactose was condensed with phenol in the presence of zinc chloride [3] under reduced pressure [6] to give an approximately 7 : 3 mixture of phenyl tetra-*O*-acetyl-α- and -β-D-galactopyranosides; its resolution by recrystallisation is wasteful,[2] while fractionation of the de-*O*-acetylation products is frustrated by the crystallisation of phenyl α-D-galactopyranoside as a molecular compound with its β-anomer.[7] However,

[1] Courtois, Proc. 4th Internat. Congr. Biochem., Vienna, 1959, Vol. I, p. 140.
[2] Helferich and Bredereck, *Annalen*, 1928, **465**, 166.
[3] Helferich and Schmitz-Hillebrecht, *Ber.*, 1933, **66**, 378.
[4] Anagnostopoulos, Courtois, and Petek, *Arch. Sci. biol., Italy*, 1955, **39**, 631.
[5] Hudson and Parker, *J. Amer. Chem. Soc.*, 1915, **37**, 1589.
[6] Shishido, *J. Soc. Chem. Ind., Japan*, 1936, **39**, 217; *Chem. Abs.*, 1936, **30**, 7118.
[7] Helferich, *Ber.*, 1944, **77**, 194.

we have taken advantage of the fact that while phenyl α- and β-D-galactopyranosides are both converted by alkali into 1,6-anhydro-β-D-galactopyranose, the β-anomer reacts thus much faster.[8] Accordingly, simultaneous de-*O*-acetylation of the mixture of acetates and complete conversion of the β-anomer into the sugar anhydride was accomplished when the mixture was treated with alkali. Excellent separation of 1,6-anhydro-β-D-galactopyranose from phenyl α-D-galactopyranoside was then achieved by chromatography on charcoal. The yield of pure galactoside in this second reaction was 56%, or 80% based on the calculated content of the α-anomer in the mixture of the acetates. The overall yield of the galactoside from penta-*O*-acetyl-β-D-galactose was 47%.

Experimental.—Methods. All solutions were evaporated under reduced pressure below 40°. Paper partition chromatography was carried out on Whatman no. 3MM paper with the following solvent systems (*a*) butan-1-ol–acetic acid–water (4 : 1 : 5, v/v),[9] and ethyl acetate–pyridine–water (10 : 4 : 3, v/v).[10] Papers were sprayed with the silver nitrate–sodium hydroxide reagent.[11]

Synthesis of phenyl α-D-galactopyranoside. A mixture of penta-*O*-acetyl-β-D-galactose {m. p. 142—144°, $[\alpha]_D^{20}$ +23° (in $CHCl_3$; *c* 1·6)} (111 g.), phenol (100 g.), and freshly fused zinc chloride (25 g.) was heated at 120° ± 5° under a water-pump vacuum for 2·5 hr. After the mixture had cooled, benzene (1 l.) was added. The pink precipitate was removed on the centrifuge and washed with benzene (100 ml.). The clear colourless supernatant liquids were washed first with water (150 ml.) and then with ice-cold 5% (w/v) aqueous sodium hydroxide (5 × 150 ml.), washed again with water until free from alkali, and dried ($CaCl_2$). When the benzene was removed *in vacuo* on a water-bath, spontaneous crystallisation gave a mixture of phenyl tetra-*O*-acetyl-α- and -β-D-galactopyranoside (102 g., 85%) having $[\alpha]_D^{17}$ +124° (in $CHCl_3$; *c* 3). Deacetylation of a sample revealed phenyl galactoside and a trace of galactose.

The mixed acetates (100 g.) were suspended in 1·3N-potassium hydroxide (3·5 l.) and heated on a boiling-water bath for 18 hr. (dissolution was complete in 0·5 hr.). The mixture was cooled in an ice-bath, neutralised to pH 6·4 with 6N-sulphuric acid with stirring, and adsorbed on a column (87 × 7·6 cm.) of equal parts by weight of B.D.H. activated charcoal powder and Celite 535,[12] which had previously been washed with water to remove acidic impurities. Fractions were collected (500 ml. each) and the optical rotations of each fraction determined. The column was eluted with water (8 l.) until sulphate was removed and then by gradient elution with aqueous ethanol (V = 20 l. and X = 0·5 in the formula of Alm, Williams, and Tiselius [13]).

The second peak of optically active material (fractions nos. 18—35) was due to 1,6-anhydro-β-D-galactopyranose (8·5 g.) mixed with traces of unidentified oligosaccharides. Recrystallisation from aqueous ethanol gave a chromatographically pure compound, softening at 155° and melting at 222—224°, $[\alpha]_D^{20}$ −21·3° (in H_2O; *c* 1·1) {lit.,[8] m. p. 221°, $[\alpha]_D$ −22° (in H_2O; *c* 2)}.

The third peak (fractions nos. 39—43), at about 10% ethanol, was due to a mixture (323 mg.) of oligosaccharides and had $[\alpha]_D^{19}$ +122° (in H_2O; *c* 1·3).

Pure phenyl α-D-galactopyranoside was obtained on concentration of the eluate of the fourth peak (fractions nos. 57—91), at 25—30% ethanol. The solid residue was extracted with hot ethanol and filtered; on slow evaporation phenyl α-D-galactopyranoside monohydrate (36 g., 55·8%) was obtained, having m. p. 143—145°, $[\alpha]_D^{22}$ +196 (in H_2O; *c* 0·6). A sample dehydrated *in vacuo* at 85° for 2 days had m. p. 143—145°, $[\alpha]_D^{20}$ +214° (in H_2O; *c* 1·4) (lit.,[3] m. p. 143—145°, $[\alpha]_D^{23}$ +213°).

The α-galactoside was completely hydrolysed by the α-galactosidase of brewer's bottom yeast,[14] and was quantitatively recovered from charcoal with 25% (v/v) aqueous ethanol.

[8] Montgomery, Richtmyer, and Hudson, *J. Amer. Chem. Soc.*, 1943, **65**, 3.
[9] Partridge, *Biochem. J.*, 1948, **42**, 238.
[10] Whistler and Hickson, *Analyt. Chem.*, 1955, **27**, 1514.
[11] Trevelyan, Procter, and Harrison, *Nature*, 1950, **166**, 444.
[12] Whistler and Durso, *J. Amer. Chem. Soc.*, 1950, **72**, 677.
[13] Alm, Williams, and Tiselius, *Acta Chem. Scand.*, 1952, **6**, 826.
[14] Clancy and Whelan, forthcoming paper.

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689. *Organogermanium Compounds. Part II.*[1] *The Preparation of Triethyl*-m- *and* -p-*nitrophenylgermane.*

By C. EABORN, K. LEYSHON, and K. C. PANDE.

TRIMETHYL-*p*-NITROPHENYLSILANE was prepared in high yield by nitrodesilylation of *p*-bistrimethylsilylbenzene by nitric acid in refluxing acetic anhydride.[2] We have now obtained the first (nitroaryl)germanium compounds, triethyl-*m*- and -*p*-nitrophenylgermane, by the analogous reaction, nitrodegermylation, of *m*- and *p*-bistriethylgermylbenzene with nitric acid in acetic acid–acetic anhydride at 100°. The yields (51 and 63%) were lower than from nitrodesilylation, partly because smaller quantities of the germanium compounds were taken and mechanical losses during fractionation were thus more serious.

Acid-cleavage of one aryl–$GeEt_3$ bond of bistriethylgermylbenzene, followed by nitration of the triethylphenylgermane produced, would cause contamination of the desired products by isomeric compounds. For the following reasons, we believe that the materials we have made are free from isomers: (i) Within the limits of the pressure control, the products boiled at a constant temperature during fractionation, and no significant amount of material boiled close to the main fraction. The fractionation was probably efficient enough to have revealed the presence of any triethyl-*o*-nitrophenylgermanes. (ii) If any triethylphenylgermane were formed, it would undergo both acid-cleavage (to give benzene which would then be nitrated to nitrobenzene) and nitrodegermylation (again to give nitrobenzene) almost as readily as does *m*- or *p*-bistriethylgermylbenzene. No nitrobenzene was detected in the products. (iii) Under the conditions used, nitrodesilylation of aryltrimethylsilanes occurs to the exclusion of acid-cleavage (protodesilylation),[3] and cleavages of aryl–Ge bonds show close similarity to those of aryl–Si bonds.[4]

Experimental.—A precision-made Vigreux column (*ca.* 18 theoretical plates) was used for fractionation.

p-*Bistriethylgermylbenzene.* From bromotriethylgermane (11 g.) and the aryl-lithium from *p*-bromophenyltriethylgermane (17 g.) and lithium (2 g.) in ether (75 ml.), there was obtained, by the usual procedure,[1] p-*bistriethylgermylbenzene* (17·5 g., 90%), b. p. 157—158°/2—3 mm., n_D^{20} 1·5218 (Found: C, 54·9; H, 8·6. $C_{18}H_{34}Ge_2$ requires C, 54·7; H, 8·7%).

m-*Bistriethylgermylbenzene.* A mixture of *m*-chlorophenyltriethylgermane (21·5 g.) and bromotriethylgermane (20 g.) was added to sodium (4 g.) in boiling toluene (120 ml.). The mixture was refluxed and stirred for 4 hr., and then filtered. The filtrate was fractionated to give m-*bistriethylgermylbenzene* (16 g., 64%), b. p. 149°/1·8 mm., n_D^{20} 1·5177 (Found: C, 54·6; H, 8·7%). A liquid (10 g.), b. p. 93—95°/2 mm., was also obtained.

Triethyl-m- *and* -p-*nitrophenylgermane.* To a stirred solution of *p*-bistriethylgermylbenzene (13·7 g.) in acetic acid (40 g.) kept at 100°, a solution of nitric acid (6·3 g. of 70% acid; 0·07 mole) in acetic anhydride (30 g.) was added dropwise at such a rate as to keep the mixture at 100°

[1] Part I, Eaborn and Pande, *J.*, 1960, 3200.
[2] Deans and Eaborn, *J.*, 1957, 498.
[3] Leyshon, unpublished work.
[4] Eaborn and Pande, *J.*, in the press.

(±5°). The mixture was kept at 100° for a further 6 hr., and then was cooled and added to a solution of sodium hydroxide (70 g.) in water (400 ml... Ether extraction followed by washing, drying (Na_2SO_4), and fractionation of the extract gave *triethyl*-p-*nitrophenylgermane* (6·1 g., 63%), b. p. 118—120°/0·3 ± 0·1 mm., n_D^{20} 1·5410 (Found: C, 51·6; H, 6·9; N, 4·7. $C_{12}H_{19}O_2NGe$ requires C, 51·2; H, 6·8; N, 5·0%).

From *m*-bistriethylgermylbenzene (15·2 g.) there was similarly obtained *triethyl*-m-*nitrophenylgermane* (5·5 g., 51%), b. p. 122—124°/0·5—0·6 mm., n_D^{20} 1·5365 (Found: C, 51·4; H, 6·8; N, 4·8%).

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