NOTES.

90. *The Preparation of 2-Acyl-3-oxo-4 : 5-benzo-1 : 2-thiazoline 1 : 1-Dioxides (N-Acylsaccharins) for the Identification of Monocarboxylic Acids.*

By Edith Stephen and Henry Stephen.

N-Acyl derivatives of saccharin are useful for the identification of monocarboxylic acids since they are rapidly prepared in small quantities by condensing acid chlorides with sodium saccharin. They are easily purified by crystallisation and have definite melting points.

Experimental.—Anhydrous sodium saccharin is obtained by dissolving saccharin (18·3 g., 1 mol.) in ethanol (170 c.c.) and adding a solution of sodium ethoxide (from 2·3 g. of sodium in 50 c.c. of ethanol). The precipitate of the sodium salt is filtered off and dried.

Preparation of the N-acyl derivatives. The acid (0·5 g., 1 mol.) is warmed with thionyl chloride (1·5 mol.) until dissolved and conversion into the acid chloride completed. Excess of thionyl chloride is removed under reduced pressure, and the chloride without further purification is treated with sodium saccharin (1·25 mol.). The mixture liquefies when heated for 3 min. and solidifies on cooling. The solid product is triturated with sodium hydrogen carbonate

solution and filtered off and the residue consisting of the *N*-acyl derivative is crystallised from methanol or ethyl methyl ketone. The yield is almost quantitative. The *N*-acylsaccharin derivatives in the Table were prepared as above.

N-Acylsaccharin	M. p.	Formula	Found (%) N	Found (%) S	Rqd. (%) N	Rqd. (%) S
Acetyl	196°		(known compound)			
Propionyl	212	$C_{10}H_9O_4NS$	5·82	13·0	5·81	12·33
Butyryl	170	$C_{11}H_{11}O_4NS$	5·5	12·8	5·51	12·6
*iso*Butyryl	158	$C_{11}H_{11}O_4NS$	5·45	12·9	5·51	12·6
Valeryl	115	$C_{12}H_{13}O_4NS$	5·15	12·2	5·25	12·0
*iso*Valeryl	137	$C_{12}H_{13}O_4NS$	5·35	12·3	5·25	12·0
Hexanoyl	92	$C_{13}H_{15}O_4NS$	4·95	11·7	5·0	11·4
Heptanoyl	85	$C_{14}H_{17}O_4NS$	4·8	11·1	4·75	10·8
Octanoyl	104	$C_{15}H_{19}O_4NS$	4·4	10·1	4·5	10·3
Nonanoyl	112	$C_{16}H_{21}O_4NS$	4·29	10·2	4·33	9·9
Decanoyl	91	$C_{17}H_{23}O_4NS$	4·2	9·7	4·15	9·5
Dodecanoyl	94	$C_{19}H_{27}O_4NS$	3·9	8·4	3·8	8·8
Tetradecanoyl	96	$C_{21}H_{31}O_4NS$	4·1	9·5	3·99	9·1
Hexadecanoyl	100·5	$C_{23}H_{35}O_4NS$	3·75	8·6	3·7	8·4
Octadecanoyl	103	$C_{25}H_{39}O_4NS$	3·6	7·8	3·5	8·1
Benzoyl	165		(known compound)			
o-Toluoyl	169	$C_{15}H_{11}O_4NS$	4·6	10·9	—	—
m- ,,	137	,,	4·7	10·8	4·65	10·6
p- ,,	182	,,	4·7	10·4	—	—
o-Chlorobenzoyl	196	$C_{14}H_8O_4NClS$	4·4	10·2	—	—
m- ,,	154	,,	4·4	10·3	4·36	10·0
p- ,,	205	,,	4·4	9·8	—	—
Phenylacetyl	182	$C_{15}H_{11}O_4NS$	4·7	9·6	4·62	9·6
1-Naphthoyl	171	$C_{18}H_{11}O_4NS$	4·2	9·8	4·15	9·5
2- ,,	183	,,	4·2	9·7	4·15	9·5
p-Anisoyl	138	$C_{15}H_{11}O_5NS$	4·5	10·4	4·4	10·1
o-Methoxybenzoyl	192	,,	4·5	10·4	4·4	10·1
Veratroyl	202	$C_{16}H_{13}O_6NS$	4·0	9·6	4·0	9·2
Phenoxyacetyl	176	$C_{15}H_{11}O_5NS$	4·5	10·4	4·4	10·1

Sulphur determinations were done with a Parr bomb.

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91. *Thermal Decomposition of the Mercuric and Silver Salts of the Isomeric Methyl Hydrogen 3-Nitrophthalates.*

By P. S. MAYURANATHAN.

THE intention of this work was to settle the structure of the isomeric half-esters of 3-nitrophthalic acid by elimination of the free carboxyl group. Gonclaves and Brown [1] proved that the isomers are definite compounds and not dimorphic forms of the same compound.

2-Methyl 1-hydrogen, m. p. 153°, and 1-methyl 2-hydrogen 3-nitrophthalate, m. p. 163°, are usually designated the α- and the β-ester respectively. Miller [2] first prepared them; Wegscheider and Lipschitz [3] established the structures quoted and determined the electrical conductivities (β, κ $1{\cdot}6 \times 10^{-2}$; α, κ $0{\cdot}2 \times 10^{-2}$); although later work [4] bore out the structural assignments there is some uncertainty and it seemed desirable to establish them unambiguously by a direct step, and the elimination of the free carboxyl group by pyrolysis seemed suitable. For this an analogy was found in the decomposition of mercuric 2 : 4 : 6-trinitrobenzoate and related alkyl derivatives by Kharasch and his co-workers.[5]

[1] Goncalves and Brown, *J. Org. Chem.*, 1952, **18**, 4.
[2] Miller, *Annalen*, 1881, **208**, 227.
[3] Wegscheider and Lipschitz, *Monatsh.*, 1900, **21**, 781.
[4] Kahn, *Ber.*, 1902, **35**, 3857; Chapman and Stephens, *J.*, 1925, **127**, 1791; Curtius and Sampler, *Ber.*, 1913, **46**, 162; Underwood and Wakeman, *J. Amer. Chem. Soc.*, 1931, **53**, 1839.
[5] Kharasch, *ibid.*, 1921, **43**, 2238; Kharasch and Griffin, *ibid.*, 1925, **47**, 1951; Kharasch and Staveley, *ibid.*, 1923, **45**, 1969.

Acid-catalysed esterification gave nearly 70% of the β-ester, and the anhydride–alcohol method in the presence of pyridine gave 90% of the α-ester. The esters were purified by using benzene in which only the α-ester is readily soluble. The mercuric salts of the α- and β-ester decomposed smoothly at 185° and 190° respectively and both gave di-(2-methoxycarbonyl-6-nitrophenyl)mercury with elimination of the theoretical amount of carbon dioxide. In both cases, the product, on treatment with potassium perbromide or periodide, gave methyl 2-bromo- or 2-iodo-3-nitrobenzoic acid respectively, which on hydrolysis afforded the easily identified acids; direct hydrolysis of both mercurial products gave *m*-nitrobenzoic acid. Clearly one ester had been transformed into the other during pyrolysis.

The silver salts underwent exothermic decomposition and gave poor yields of methyl *m*-nitrobenzoate.

Gonclave and Brown [1] reported the conversion of the α- and the β-ester when it was heated in quinoline, for which they assume the possibility of a transition through the anhydride due to intermediate salt formation. In the present case the reaction may be ionic and probably takes place through the oxonium complex corresponding to the anhydride.

Experimental.—1-Methyl 2-hydrogen 3-nitrophthalate (β-ester), m. p. 163°, was prepared by the method of Cohen, Woodroffe, and Anderson; [6] 2-methyl 1-hydrogen 3-nitrophthalate (β-ester), m. p. 153°, by Miller's method.[1]

Mercuric salt of the α-ester. The α-ester (25 g.), dissolved in sodium carbonate solution (4·6 g. in 15 c.c.), was treated with mercuric acetate (34 g.) in water (200 c.c.) and acetic acid (2 c.c.). The precipitated *salt* (34 g.) was filtered off, washed with water and alcohol, dried on a porous plate, and kept in a desiccator away from light and air; it could not be crystallised (Found: Hg, 30·8. $C_{18}H_{12}O_{12}N_2Hg$ requires Hg, 31·35%).

The salt (20 g.) was heated at 180°, evolution of carbon dioxide being complete (loss in wt., 12·9%) in 5—6 hr. The crystalline residue of di-(2-methoxycarbonyl-6-nitrophenyl)mercury, m. p. 190°, was insoluble in all solvents tried (Found: Hg, 37·1. Calc. for $C_{16}H_{12}O_6N_2Hg$: Hg, 36·4%).

This product (2 g.) was heated in 2N-sodium hydroxide on a water-bath for 1 hr., most of it dissolving. The mixture was filtered and the filtrate acidified, a flocculent precipitate appearing which did not melt at 360°. Heating this material (1 g.) with concentrated hydrochloric acid (10 c.c.) under reflux, collecting the crystals that separated, and recrystallising them from water gave *m*-nitrobenzoic acid, m. p. and mixed m. p. 140°.

Heating the mercury compound (10 g.) with 2M-potassium perbromide on a water-bath for 1 hr., removing the free bromine by evaporation, collecting the product that separated, taking it up in ether, washing it with aqueous sodium thiosulphate, drying ($MgSO_4$), and evaporating gave *methyl 2-bromo-3-nitrobenzoate* which crystallised from dilute methyl alcohol as needles (6 g.), m. p. 77° (Found: C, 36·8; H, 2·5; N, 5·3; Br, 30·6. $C_8H_6O_4NBr$ requires C, 36·8; H, 2·3; N, 5·4; Br, 30·8%).

Similar treatment of the mercury compound with potassium periodide gave *methyl 2-iodo-3-nitrobenzoate* (6 g.), needles, m. p. 61° (Found: C, 31·6; H, 2·5; N, 4·5; I, 41·2. $C_8H_6O_4NI$ requires C, 31·3; H, 2·0; N, 4·6; I, 41·4%), hydrolysed by sulphuric acid to 2-iodo-3-nitrobenzoic acid, prismatic needles, m. p. 205° alone or mixed with a specimen made by the method of Whitmore *et al.*[7]

β-Ester. The β-ester (20 g.) was converted into its *mercuric salt* as above (Found: Hg, 31·1. $C_{18}H_{12}O_{12}N_2Hg$ requires Hg, 31·35%). Decomposition, which began only at 190°, was complete in 5 hr. The product and derived compounds were the same as from the α-ester, mixed m. p.s in appropriate cases being undepressed. Analyses were performed on the Hg derivative (Found: Hg, 37·1. Calc. for $C_{16}H_{12}O_8N_2Hg$: Hg, 36·4%), bromo-ester (Found: C, 36·8; H, 2·5; N, 5·3; Br, 30·6%), and iodo-ester (Found: C, 31·6; H, 2·5; N, 4·5; I, 41·2%).

Silver salts. The α-ester (5 g.) was dissolved in the minimum amount of dilute aqueous ammonia and added to silver nitrate (5 g.) in water (2 c.c.). The flocculent precipitated *salt* (8 g.) was dried at 100° (Found: Ag, 32·0. $C_8H_6O_6NAg$ requires Ag, 32·5%). The salt (5 g.) decomposed exothermally at 230°. The reaction could not be controlled and most of the product was lost. The small residue was extracted with ether, washed with water, dried,

[6] Cohen, Woodroffe, and Anderson, *J.*, 1916, 222.
[7] Whitmore, Culhane, and Nahu, *Org. Synth.*, 1927, **7**, 1.

recovered, and crystallised from dilute methyl alcohol, giving needles (1 g.), m. p. 68°. Hydrolysis with concentrated hydrochloric acid (15 c.c.) gave *m*-nitrobenzoic acid, m. p. and mixed m. p. 141°. The silver salt of the β-ester behaved similarly.

The author is indebted to Mr. P. Ramaswamy Iyer, formerly of the Indian Institute of Science, Bangalore, for suggesting the problem and for guidance, and to the late Sir M. O. Forster for encouragement.

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92. *Thermal Decomposition of Mercuric* o- *and* m-*Nitrobenzoate and* 4-*Nitrophthalate.*

By P. S. Mayuranathan.

Mercuric benzoate, when heated at 170°, gives a mercurated acid; [1] the same compound is formed by heating mercuric phthalate.[2] When pyrolysed, mercuric salts of nearly all organic acids evolve carbon dioxide and in some cases are a convenient method for linking mercury to carbon, particularly in the aromatic series. *E.g.*, mercuric 2 : 4 : 6-trinitrobenzoate [3] and the methyl hydrogen 3-nitrophthalates [4] decompose quantitatively at 190° to carbon dioxide and the corresponding diphenylmercury derivatives. The influence of nitro- and carboxy-groups on the decomposition has now been studied for mercury salts of the isomeric nitrobenzoic acids and nitrophthalic acids—that of *p*-nitrobenzoic acid [5] and 3-nitrophthalic acid [6] had previously been reported.

Mercuric *o*-nitrobenzoate decomposed at 180° to carbon dioxide and di-(2-nitrophenyl)-mercury, as on halogenation by potassium perbromide or periodide the product gave *o*-bromo- and *o*-iodonitro-benzene respectively. Mercuric *m*-nitrobenzoate did not decompose but gave anhydro-2-hydroxymercuri-3-nitrobenzoic acid. This was obtained before by Whitmore *et al.*[5, 6] on heating mercuric 3-nitrophthalate, as on treatment with potassium perbromide or periodide it yielded 2-bromo- or 2-iodo-3-nitrobenzoic acid respectively. Mercuric *p*-nitrobenzoate [5] underwent mercuration to give anhydro-2-hydroxymercuri-4-nitrobenzoic acid, as it yielded on halogenation 2-bromo- and 2-iodo-4-nitrobenzoic acid. Mercuric 4-nitrophthalate eliminated carbon dioxide (cf. the 3-nitrophthalate) at 200°, to give the same product as was obtained from *p*-nitrobenzoic acid (II).

Experimental.—Di-(o-*nitrophenyl*)*mercury.* Mercuric *o*-nitrobenzoate (18 g.) was heated at 180° until elimination of carbon dioxide was complete (4 hr.). The brownish crystalline residue of mercurial was insoluble in organic solvents (yield 16%) (Found: Hg, 46·3. Calc. for $C_{12}H_8O_4N_2Hg$: Hg, 45·0%).

This derivative (4 g.) was heated with 2M-potassium perbromide and periodide (20 c.c.) severally on a water-bath for 1 hr. The resulting oils were freed from halogen by washing them with thiosulphate and crystallised from benzene, giving 1 g. of *o*-bromonitrobenzene, m. p. 39°, and of *o*-iodonitrobenzene, m. p. 49°, respectively. Mixed m. p.s with authentic specimens were undepressed.

Anhydro-2-hydroxymercuri-3-nitrobenzoic acid. Mercuric *m*-nitrobenzoate (10 g.) was heated at 190° for 6 hr. but there was no loss in weight. The *product* was washed several times with water and alcohol to remove the free acid. It did not melt when heated (Found: Hg, 55·3. $C_7H_3O_4NHg$ requires Hg, 54·8%). It dissolved in warm alkali.

The anhydro-mercuri-compound (5 g.) was treated with potassium perbromide or periodide as above. The solution was then evaporated to remove the excess of the halogen, acidified, and

[1] Dimroth, *Ber.*, 1902, **75**, 2870; Whitmore, "Organic Compounds of Mercury," Chemical Catalog Co., New York, 1921, pp. 35, 290.
[2] Pesci, *Atti R. Accad. Lincei*, 1901, V, **10**, 362.
[3] Kharasch, *J. Amer. Chem. Soc.*, 1925, **47**, 1948.
[4] Mayuranathan, preceding paper.
[5] Whitmore, *J. Amer. Chem. Soc.*, 1922, **44**, 1546.
[6] Whitmore, Culhane, and Nahu, *Org. Synth.*, 1927, **7**, 1; Culhane, *ibid.*, p. 12; Whitmore and Culhane, *J. Amer. Chem. Soc.*, 1929, **51**, 604.

extracted with ether. The ethereal solution was washed with thiosulphate, dried, and evaporated. Crystallisation from benzene gave 1 g. of the bromo- and iodo-nitrobenzoic acid, m. p. 185° and 205°, respectively. M. p.s were undepressed on admixture with 2-bromo- and 2-iodo-3-nitrobenzoic acids prepared by the method of Whitmore *et al.*[6]

Anhydro-2-hydroxymercuri-4-nitrobenzoic acid. 4-Nitrophthalic acid was prepared and purified according to the method of Wegscheider and Lipschitz [7] (after removal of 3-nitrophthalic acid). The acid (23 g.) was dissolved in a solution of sodium carbonate (16 g.) in water (20 c.c.) and treated with mercuric acetate (45 g.) in water (150 c.c.) containing acetic acid (1 c.c.). The precipitate was washed several times with water and alcohol : it did not melt (Found : Hg, 63·2. Calc. for $C_8H_3O_6NHg$ requires Hg, 49·0%).

The salt (20 g.) was heated at 190° for 6 hr. (loss in wt., 6·5. Calc. for $C_7H_2O_4NHg{\cdot}CO_2H$: CO_2, 7·4%). The product was washed several times with water and alcohol. It did not melt (Found : Hg, 54·8. Calc. for $C_7H_3O_4NHg$: Hg, 55·0%).

Bromination and iodination as above gave 2-bromo- and 2-iodo-4-nitrobenzoic acid identified as above. Hydrolysis gave *p*-nitrobenzoic acid.

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[7] Wegscheider and Lipschitz, *Monatsh.*, 1900, **21**, 781.

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93. *The Action of Hydrogen Chloride on the Nickel and Palladium Derivatives of Dimethylglyoxime.*

By A. G. SHARPE and D. B. WAKEFIELD.

HYDROGEN CHLORIDE combines with the nickel derivative of dimethylglyoxime, $Ni(DH)_2$,* yielding a blue-grey product of formula $Ni(DH)_2,2HCl$.[1] This substance is decomposed by, or is insoluble in, all common solvents except acetone, in which it is sparingly soluble; the solution decomposes slowly even at room temperature, but from the fact that on electrolysis hydrogen and bisdimethylglyoxime nickel are liberated at the cathode Paneth and Thilo [1] deduced that the structure of the compound is $[Ni(DH_2)_2]Cl_2$. This formula has been discussed subsequently,[2,3] but no further work on the compound has been reported.

The blue colour of the complex suggests the presence of tetrahedrally or octahedrally co-ordinated nickel (for reviews of the stereochemistry of nickel see refs. 4 and 5). The magnetic moment (3·07 B.M.) is compatible with either arrangement (the prediction of crystal-field theory that tetrahedral complexes should have moments of 3·3 B.M. or more has not, in the opinion of the authors, received sufficient experimental confirmation for a distinction between octahedral and tetrahedral arrangements to be made), but not with the presence of planar four-co-ordinated nickel involving the usual $3d4s4p^2$ orbitals. Its solution in acetone, however, reacts only very slowly with silver nitrate in this solvent; and its conductivity, which increases with time, is less than one twentieth of that of an equimolecular acetone solution of barium iodide. These observations suggest that the small conductivity is due to incipient decomposition, and that the correct formulation of the compound is $[Ni(DH_2)_2Cl_2]$; the most likely configuration seems to be an octahedral one with dimethylglyoxime functioning as a bidentate ligand and with chlorine atoms occupying *trans*-positions, but in this instance the assignment of configuration would be a difficult matter and has not been attempted. When treated with acetyl chloride, the compound yields a pale-green diacetyl derivative, which is also paramagnetic ($\mu = 3{\cdot}24$

* In this communication DH_2 = dimethylglyoxime.

[1] Paneth and Thilo, *Z. anorg. Chem.*, 1925, **147**, 196.
[2] Hieber and Leutert, *Ber.*, 1927, **60**, 2296.
[3] Thilo and Heilborn, *Ber.*, 1931, **64**, 1441.
[4] Nyholm, *Chem. Rev.*, 1953, **53**, 263.
[5] *Idem, Quart. Rev.*, 1953, **7**, 377.

B.M.) and a non-conductor in acetone solution; this substance therefore has the constitution $[Ni(DH{\cdot}CO{\cdot}CH_3)_2Cl_2]$.

Bisdimethylglyoxime palladium(II) shows analogous reactions: addition of hydrogen chloride produces the pale yellow compound $[Pd(DH_2)_2Cl_2]$, which on acetylation gives the diacetyl derivative $[Pd(DH{\cdot}CO{\cdot}CH_3)_2Cl_2]$. Both of these substances, unlike the nickel compounds, are diamagnetic; this difference is, however, typical of the magnetic properties of analogous compounds of metals of the first and of later transition series, which is discussed elsewhere.[5,6]

Experimental.—Hydrogen chloride addition products were made as described for the nickel compound by Paneth and Thilo [1] (Found, for the Ni compound: Ni, 16·1; Cl, 18·9; C, 26·5; H, 4·6; N, 14·9. Calc. for $C_8H_{16}O_4N_4Cl_2Ni$: Ni, 16·2; Cl, 19·6; C, 26·5; H, 4·4; N, 15·5%. Found, for the Pd *compound*: C, 23·7; H, 3·7; N, 13·9; Cl, 18·1. $C_8H_{16}O_4N_4Cl_2Pd$ requires C, 23·4; H, 3·9; N, 13·6; Cl, 17·3%).

For the preparation of the *acetyl derivative*, bisdimethylglyoxime nickel was shaken with acetyl chloride at room temperature during 15 hr., or heated under reflux with the reagent during 1 hr. The product was freed from excess of acetyl chloride by drying *in vacuo* (Found: Ni, 13·2; C, 32·0; H, 4·9; N, 12·0; Cl, 15·6; $CH_2{\cdot}CO$, 20·9. $C_{12}H_{20}O_6N_4Cl_2Ni$ requires Ni, 13·2; C, 32·4; H, 4·5; N, 12·6; Cl, 15·9; $CH_3{\cdot}CO$, 19·3%). Bisdimethylglyoxime palladium was acetylated by shaking it with acetyl chloride at room temperature (heating resulted in decomposition) (Found, for the *diacetyl derivative*: C, 28·9; H, 4·0; N, 28·9; Cl, 14·4. $C_{12}H_{20}O_6N_4Cl_2Pd$ requires C, 28·6; H, 4·0; N, 28·6; Cl, 14·4%).

Comparison of conductivities was made by using the apparatus of Haszeldine and Woolf; [7] magnetic susceptibilities were determined by the Gouy method, the balance at University College, London, being used by kind permission of Professor R. S. Nyholm.

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[6] *E.g.*, van Vleck, "Theory of Electric and Magnetic Susceptibilities," Oxford, 1932; Nyholm and Sharpe, *J.*, 1952, 3579; Owen, *Discuss. Faraday Soc.*, 1955, **19**, 127.
[7] Haszeldine and Woolf, *Chem. and Ind.*, 1950, 544.

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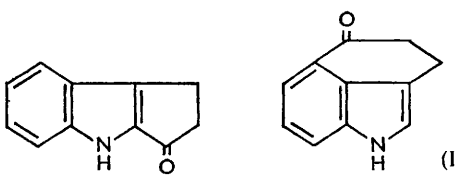
94. *New Synthesis of* 2 : 3-*Dihydro*-1-*oxopentindole.*

By K. F. JENNINGS.

2 : 3-DIHYDRO-1-OXOPENTINDOLE (I) was obtained in low yield by the addition of phosphoric oxide to a solution of β-3-indolylpropionic acid in refluxing xylene. This resulted from an attempt to produce 1 : 3 : 4 : 5-tetrahydro-5-oxobenz(*c*,*d*)indole (II) more simply,[1] and represents a new synthesis of the pentindole skeleton.[2,3] When β-3-indolylpropionic



(I) (II)

acid was treated with anhydrous hydrogen fluoride, boron trifluoride–ether, or phosphoric oxide–orthophosphoric acid, only decomposition products resulted. Similarly, β-(2-acetyl-3-indolyl)propionic acid with anhydrous hydrogen fluoride gave no pure product.

Experimental.—2 : 3-*Dihydro*-1-*oxopentindole.* To a refluxing solution of β-3-indolylpropionic acid (1·0 g.) in xylene (200 ml.) was added portionwise during 30 min., phosphoric oxide (8 g.). After further refluxing (1 hr.), the tarry decomposition products were filtered off, and

[1] Grob and Hofer, *Helv. Chim. Acta*, 1952, **35**, 2095; Uhle, *J. Amer. Chem. Soc.*, 1949, **71**, 761; Kornfeld, Fornefeld, Kline, Mann, Morrison, Jones, and Woodward, *ibid.*, 1956, **78**, 3097.
[2] Elks, *J.*, 1944, 624.
[3] Manske, *Canad. J. Res.*, 1931, **4**, 595.

the solution was concentrated to yield 2 : 3-dihydro-1-oxopentindole (0·1 g., 11%) as short yellow needles, m. p. 242—242·5°. Recrystallisation from ethanol raised the m. p. to 252—252·5° (lit., 249°,[2] 248°[3]) (Found : C, 77·1; H, 5·4. Calc. for $C_{11}H_9ON$: C, 77·2; H, 5·3%). In methanol, it absorbs at 2340 and 3000 Å (ε 20,870, and 28,170 respectively) and, in the infrared region (potassium bromide pellet), at 2·86(w), 3·10(w), (OH, >NH), and 6·02(s) μ (αβ-unsaturated C=O).

Methyl β-(2-*acetyl*-3-*indolyl*)*propionate*. Freshly fused zinc chloride (1·0 g.) was added to a solution of methyl β-3-indolylpropionate [4] (2·0 g.) in acetyl chloride (20 g.). After 10 min. at room temperature the dark solution was poured on crushed ice (100 g.) and set aside for 3 hr., and thrice extracted with ether; the extracts were washed with aqueous sodium carbonate, and water, and dried (Na_2SO_4); removal of the solvent gave *methyl* β-(2-*acetyl*-3-*indolyl*)*propionate* (1·74 g., 74%), m. p. 87—88°. Recrystallisation from ether yielded small tetrahedra of the same m. p. (Found : C, 69·0; H, 6·5. $C_{14}H_{15}O_3N$ requires C, 68·6; H, 6·5%). In methanol, it has max. at 2350 and 3100 Å (ε 8340 and 15,600 respectively).

β-(2-*Acetyl*-3-*indolyl*)*propionic acid*. The above ester (1·6 g.) was dissolved in 10% potassium hydroxide in 90% ethanol (20 ml.) and refluxed for 1 hr. Ethanol was removed on the water-bath, water (20 ml.) was added, and the solution made acid to Congo-red with concentrated hydrochloric acid. Extraction with chloroform, washing of the extracts with water, drying (Na_2SO_4), and removal of the solvent gave clusters of needles of the *acid* (1·15 g., 76%), m. p. 127—130°. Recrystallisation from water gave m. p. 125—127° (Found : N, 6·4. $C_{13}H_{13}O_3N$ requires N, 6·1%). In methanol, it has max. at 2250, 2850, 2900, and 3100 Å (ε 22,500, 5640, 6410, and 7100 respectively).

I thank Sir Robert Robinson, O.M., F.R.S., for his interest.

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[*Received, August 17th,* 1956.]

[4] Manske and Robinson, *J.*, 1927, 241.

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95. *Organosilicon Compounds. Part XIX.* Trimethyl*-p-*nitrophenylsilane.*

By F. B. DEANS and C. EABORN.

TRIMETHYL-*p*-NITROPHENYLSILANE is useful in studies of aryl–Si bonds and as a source of *p*-aminophenyltrimethylsilane and its derivatives. The *p*-nitro-compound has previously been obtained by nitration of trimethylphenylsilane with copper nitrate in acetic acid [1] or with nitric acid in acetic anhydride,[2] and is separated with difficulty from the *o*- and *m*-isomers formed along with it in similar amounts. We have now obtained it very simply in 80% yield by treating *p*-bistrimethylsilylbenzene with nitric acid in acetic anhydride, a reagent which causes little acidic cleavage of the aryl–Si bond but allows electrophilic attack by a nitronium ion or related entity on the carbon atom of this bond. (The appreciable quantities of nitrobenzene formed in nitration of trimethylphenylsilane [1,2] probably arise, at least in part, from similar attack.) When a *p*-nitro-group has been introduced the second trimethylsilyl group is not replaced by prolonged treatment with the remaining nitrating agent.

Use of Si–aryl bond-cleavage to introduce a nitro-group at a selected position in an aromatic molecule is potentially of considerable synthetic value.[3]

Experimental.—A solution of fuming (95 wt.-%) nitric acid (6 ml.) in acetic anhydride (10 ml.) was added dropwise during 1½ hr. to a boiling solution of *p*-bistrimethylsilylbenzene (5 g.) in the same solvent (14 ml.), and the cooled mixture was then added to water (100 ml.).

* Part XVIII, *J.*, 1957, 137.

[1] Benkeser and Brumfield, *J. Amer. Chem. Soc.*, 1951, **73**, 4770.
[2] Speier, *ibid.*, 1953, **75**, 2930.
[3] Cf. Chvalovsky and Bazant, *Coll. Czech. Chem. Comm.*, 1951, **16**, 580.

Ether-extraction was followed by washing of the extract with aqueous sodium hydroxide and water. After drying (Na_2SO_4), the ether was removed and the residue was taken up in light petroleum (b. p. 40—60°). The solution was passed through a column of alumina (which retained several coloured bands), and then concentrated and cooled in acetone–solid carbon dioxide, to give trimethyl-*p*-nitrophenylsilane (3·6 g., 82%), m. p. 37°, undepressed by admixture with an authentic [1] sample. An experiment in which mixing of the reactants was followed by 18 hours' boiling gave identical results.

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96. m-*Hydroxyphenylpyruvic Acid.*

By R. M. ACHESON.

THE preparation of *m*-hydroxyphenylpyruvic acid from *m*-hydroxybenzaldehyde has been reported, without details, by Flatow,[1] and later [2] by the hydrolysis of the phenyloxazolone in which its separation from benzoic acid and a difficult crystallisation owing to high solubility from water are involved. Synthesis *via* the methyloxazolone and crystallisation from nitromethane, a solvent which is also much preferable to water for *p*-hydroxyphenylpyruvic acid, gave more satisfactory results and are described.

Although the 2 : 4-dinitrophenylhydrazones of phenylpyruvic acid and its 3- and 4-hydroxy-derivatives had slightly different R_F values (0·82, 0·71, 0·75, respectively) when ascending Whatman No. 1 paper in butanol–N-aqueous ammonia–ethanol (7 : 1 : 2, by vol.) it was not possible to separate mixtures in this solvent.

Experimental.—*4-3′-Acetoxybenzylidene-2-methyloxazolone. m*-Hydroxybenzaldehyde (41·5 g.), acetylglycine (39·4 g.), sodium acetate (freshly fused; 27·2 g.), and acetic anhydride (122 ml.) were refluxed for 45 min., cooled until solidification began, and poured into vigorously stirred water (1700 ml.). Stirring was continued (¾ hr.), and the yellow precipitate (66·9 g.) collected and dried at 15° *in vacuo* ($NaOH–P_2O_5$). Rapid crystallisation from acetone (394 ml.)–water (252 ml.) gave *4-3′-acetoxybenzylidene-2-methyloxazolone* (48·7 g., 58%), m. p. 119—120°. Repeated crystallisation, involving some hydrolysis, gave yellow prisms, m. p. 122—125° (Found: C, 64·1; H, 4·8; N, 5·9. $C_{13}H_{11}O_4N$ requires C, 63·7; H, 4·5; N, 5·7%).

m-*Hydroxyphenylpyruvic acid.* The oxazolone (11·0 g.) was refluxed with N-hydrochloric acid (250 ml.) under nitrogen (1½ hr.). The filtered dark red solution was extracted with ether (4 × 250 ml.). Evaporation of the dried extract below 60° *in vacuo*, and drying in a vacuum desiccator (NaOH) gave a sticky solid (5·6 g.); two crystallisations from nitromethane then gave the acid as pale yellow needles, (1·9 g., 25%), m. p. 175° (decomp.) (Found: C, 59·9; H, 4·5. Calc. for $C_9H_8O_4$: C, 60·0; H, 4·4%). The 2 : 4-*dinitrophenylhydrazone* separated from aqueous ethanol in pale yellow prisms, m. p. 208° (Found: C, 49·8; H, 3·3; N, 15·2. $C_{15}H_{12}N_4O_7$ requires C, 50·0; H, 3·3; N, 15·6%).

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[1] Flatow, *Z. physiol. Chem.*, 1910, **64**, 380.
[2] Hahn and Werner, *Annalen*, 1935, **520**, 123.

97. *Tritium-labelled 2-Methyl-1 : 4-naphthaquinone and Confirmation of the Structure of its Adduct with Sodium Hydrogen Sulphite.*

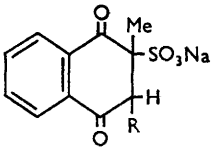
By D. H. MARRIAN.

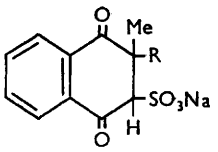
THE use of 2-methylnaphthalene-1 : 4-diol bis(disodium phosphate) as a radiosensitiser in the treatment of some malignant conditions [1] has led to studies of the metabolism of the compound labelled with ^{32}P,[2] with ^{14}C,[3] and, of a derivative, with ^{82}Br.[4] A simple method of introducing tritium into position 3 of the parent quinone is now reported.

[1] Mitchell, *Brit. J. Cancer*, 1953, **7**, 313.
[2] Neukomm, Peguiron, Lerch, and Richard, *Arch. Internat. Pharmacodyn. Therapie*, 1953, **93**, 373; Neukomm, "Radiobiology Symposium," Butterworths Scientific Publications, London, 1954, p. 189.
[3] Marrian and Maxwell, *Brit. J. Cancer*, in the press.
[4] *Idem, ibid.*, to be published.

When 2-methyl-1 : 4-naphthaquinone is shaken with aqueous sodium hydrogen sulphite, the quinone dissolves,[5] and the adduct can be isolated.[6-8] Spectral data support structure (I; R = H) for the adduct,[9] and this formulation accords with the action of alkali, which regenerates the quinone,[7] doubtless by β-elimination.[9]

When the reaction is carried out by shaking the quinone with excess of sodium pyrosulphite and tritiated water, and the resulting solution made alkaline, the recovered quinone contains tritium. The quinone was converted into 3-bromo-2-methyl-1 : 4-naphthaquinone [3, 10] which then contained no significant radioactivity, thus confirming that the tritium had occupied position 3.

(I) 



(II)

Tritium-labelled 2-methylnaphthalene-1 : 4-diol bis(disodium phosphate) was obtained by reduction and phosphorylation.[11]

The introduction of tritium by this reaction confirms structure (I; R = ^{3}H) for the adduct. The spectrally similar structure (II; R = H) was discounted by Carmack *et al.*[9] since the adduct did not aromatise easily to a naphthaquinonesulphonate; it is not likely that (II; R = ^{3}H) would give a tritium-labelled quinone by alkali treatment of the labelled adduct.

Experimental.—Tritium-labelled 2-methyl-1 : 4-naphthaquinone. 2-Methyl-1 : 4-naphthaquinone (1·7 g.) was shaken vigorously with water (10 c.c.; containing 200 μc of tritium oxide) and sodium pyrosulphite (2·0 g.) until solution was complete. A solution of sodium hydroxide (40%; 2 c.c.) was added, and the yellow precipitate stirred and rapidly filtered off. After being washed with water and then with dilute acetic acid (10%), the solid was recrystallised from a mixture of alcohol (9 c.c.) and acetic acid (1 c.c.) giving yellow needles (1·25 g.), m. p. 105—106°. The water formed on combustion of this material [12] had a specific activity of $2{\cdot}93 \times 10^{-3}$ μc/mole indicating an activity of 1·17 μc/mmole for the product.

A more convenient method for higher-activity experiments is as follows: 2-methyl-1 : 4-naphthaquinone (1·7 g.), water (5 c.c.; 100 mc of tritium oxide), and sodium pyrosulphite (2·0 g.) were warmed slightly and vigorously shaken until solution was complete. Ethyl acetate (25 c.c.; redistilled) was added and both phases were stirred rapidly during the addition of saturated lithium hydroxide (7·5 c.c.). The organic layer was washed with saturated brine containing a trace of acetic acid, dried, and evaporated to dryness. The residual quinone (almost quantitative recovery) was reduced catalytically and converted into the bis(barium phosphate) [11] and thence into a solution of the sodium salt by ion exchange. Counted as before, the compound had a specific activity of 3·82 μc/mmole or gave about 4×10^6 counts/min./mmole when counted as an indefinitely thin layer in a windowless counter.[13]

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University of Cambridge. [*Received, August 27th,* 1956.]

[5] Moore, *J. Amer. Chem. Soc.*, 1941, **63**, 2049.
[6] Baker, *ibid.*, 1942, **64**, 1096.
[7] Menotti, *ibid.*, 1943, **65**, 1209.
[8] Ablondi, *ibid.*, p. 1776.
[9] Carmack, Moore, and Balis, *ibid.*, 1950, **72**, 844.
[10] Adams, Giessman, Baker, and Teeter, *ibid.*, 1941, **63**, 533.
[11] Todd and Atherton, B.P., 674,087/1950.
[12] See Glascock, "Isotropic Gas Analysis for Biochemists," Academic Press Inc., New York, 1954.
[13] Eidinoff and Knoll, *Science*, 1951, **112**, 250.