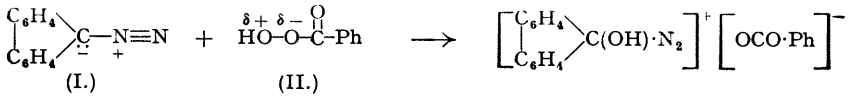
NOTES.

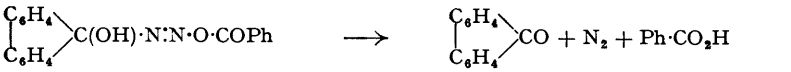
305. *Experiments with Diazomethane and its Derivatives. Part XVI. Action of Diazomethanes on Perbenzoic Acid and Benzoquinone Derivatives.*

By ALEXANDER SCHÖNBERG, WILLIAM IBRAHIM AWAD, and NAZIH LATIF.

VERY little seems to be known about the action of peracids on diazohydrocarbons. When a benzene solution containing 9-diazofluorene and perbenzoic acid is warmed, nitrogen is evolved and benzoic acid and fluorenone are formed. On the basis of a positively polarised hydroxyl group in peracids (cf. II) (Swern, *Chem. Reviews*, 1949, **45**, 1; *J. Amer. Chem. Soc.*, 1947, **69**, 1692; Derbyshire and Waters, *Nature*, 1950, **165**, 401) and the electronic formula (I) for 9-diazofluorene (cf. Eistert, "Newer Methods of Preparative Organic Chemistry," Interscience Publ., 1948, p. 514) the reaction may be formulated as follows:

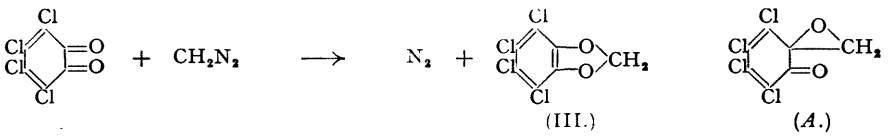


(I.) (II.)



9-Diazofluorene (the preparation of which we have improved) is a particularly suitable substance for investigation of the action of peracids, because fluorenone is markedly stable to peracids.

Continuing our work on *o*-quinones, we have investigated the action of diazomethane and diphenyldiazomethane on tetrachloro- and tetrabromo-*o*-benzoquinone, which are stable substances in contrast to *o*-benzoquinone itself. The reaction proceeded in all cases as illustrated below; for the mechanism of the reaction see Schönberg and Awad, *J.*, 1950, 72.



(III.) (*A*.)

In accordance with the proposed constitution, the reaction products are colourless or almost so, and they are rather stable towards acids. This excludes the formation of an ethylene oxide ring (as *A*); it is stated that in the case of phenanthraquinone and diazomethane two substances are formed, namely, the analogues of (III) and (*A*) respectively (Arndt, Amende, and Ender, *Monatsh.*, 1932, **59**, 210; Biltz and Paetzold, *Annalen*, 1923, **433**, 71, 81).

Experimental.—*9-Diazofluorene.* Fluorenone hydrazone (4 g.), mercuric oxide (7 g.), and anhydrous sodium sulphate (2 g.) were ground together for a few minutes, then transferred to a dry, glass-stoppered bottle, and dry ether (50 c.c.) was added. About ½ c.c. of a freshly prepared, concentrated solution of potassium hydroxide in ethyl alcohol was added, the whole shaken for five minutes by hand and then for

30 minutes on the shaker. The reaction started at once, as shown by a dark deposit formed during the hand-shaking. The solution was filtered, the residue was washed with ether, and the washings were combined with the main ethereal solution; this was then concentrated under reduced pressure, red crystals being obtained, m. p. 94—95° (yield, almost quantitative) (cf. Vogel, "Practical Organic Chemistry").

Action of perbenzoic acid on 9-diazofluorene. 9-Diazofluorene (0·5 g.) was dissolved in benzene (12 c.c.), warmed at 45°, and an ice-cold benzene solution (12 c.c.) of the peracid (0·6 gm.) added gradually (benzene, dried over sodium). Evolution of nitrogen occurred and at the end (about 20 minutes) the solution became yellowish-orange in colour. It was evaporated to dryness, the residue treated at once with sodium carbonate solution, and the mixture extracted with benzene. The aqueous layer was treated with dilute hydrochloric acid; a solid was precipitated (0·1 g.), which was crystallised from hot water and proved to be benzoic acid by m. p. and mixed m. p. determinations.

The benzene layer was dried (Na_2SO_4), the benzene driven off *in vacuo*, and the residue left *in vacuo* for 48 hours. The solid residue (0·3 g.) was recrystallised several times from dilute methyl alcohol, and the yellow crystals were proved by m. p. and mixed m. p. determinations to be fluorenone (0·15 g.).

Action of perbenzoic acid on fluorenone. This experiment was carried out with fluorenone (1·8 g.) as described for 9-diazofluorene. Fluorenone (1·1 g.) was recovered (m. p. and mixed m. p.).

3 : 4 : 5 : 6-*Tetrachloro*-1 : 2-*methylenedioxybenzene* (III). Tetrachloro-*o*-benzoquinone (Jackson and MacLaurin, *Amer. Chem. J.*, 1907, **37**, 7) (0·5 g.) in ether was allowed to react in the cold with diazomethane (from nitrosomethylurea; Arndt, *Org. Synth.*, 1935, **15**, 3). A vigorous evolution of gas was observed. After 90 minutes the ether was driven off and the residue crystallised from methyl alcohol as crystals (>80%), m. p. *ca.* 171° (Found: C, 32·3; H, 1·0. Calc. for $C_7H_2O_2Cl_4$: C, 32·3; H, 0·8%). The product was recovered unchanged when heated under reflux in dioxan (5·5 c.c.) and hydrochloric acid (*d ca.* 1·18; 1 c.c.) for 30 minutes.

3 : 4 : 5 : 6-*Tetrabromo*-1 : 2-*methylenedioxybenzene*. This substance (>80% yield) was prepared as above, from tetrabromo-*o*-quinone (Zincke, *Ber.*, 1887, **20**, 1777). It had m. p. 203° (from acetone) (Found: C, 19·7; H, 0·5; Br, 73·0. Calc. for $C_7H_2O_2Br_4$: C, 19·2; H, 0·4; Br, 73·5%).

3 : 4 : 5 : 6-*Tetrachloro*-1 : 2-(*diphenylmethylenedioxy*)*benzene*. To tetrachloro-*o*-benzoquinone (0·5 g.) in benzene was added a small excess of diphenyldiazomethane at room temperature. After 24 hours the benzene was evaporated and the residue treated with a few c.c. of methyl alcohol. A crystalline product was formed which was recrystallised from alcohol as crystals (>80%), m. p. 141° (Found: C, 55·8; H, 2·5; Cl, 34·7. Calc. for $C_{19}H_{10}O_2Cl_4$: C, 55·4; H, 2·4; Cl, 34·4%). The product was unchanged when treated with hydrochloric acid as described above.

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306. *The Reaction of Diazomethane with Stilbœstrol in the Presence of Propanol.*

By AHMED MUSTAFA.

SCHÖNBERG AND MUSTAFA (*J.*, 1946, 746) reported that stilbœstrol and diazomethane in *n*-propanol–ether gave stilbœstrol di-*n*-propyl ether, but Gerber and Curtin (*J. Amer. Chem. Soc.*, 1949, **71**, 1499) obtained the mono- and the di-methyl ether only. These are indeed, by far, the main products. Schönberg and I would like to state that, in our paper, the use of the words "recrystallisation" and "crystallised" in connection with the isolation of stilbœstrol di-*n*-propyl ether are to be replaced by "fractional crystallisation" and "fractionally crystallised" respectively.

The pure di-*n*-propyl ether is obtained (see below) in quantities enough for microanalysis, but this gives no indication of how much is actually formed. Gerber and Curtin (*loc. cit.*) also identified only 90% of their reaction products.

Experimental.—Stilbœstrol (0·5 g.) (B.D.H.) was dissolved in a mixture of ether (20 c.c.) and *n*-propyl alcohol (freshly distilled) (20 c.c.); to this cold solution, an ethereal solution of diazomethane (prepared from 10 g. of nitrosomethylurea and distilled) was added. The reaction mixture was kept for 48 hours in ice–salt, whereafter further ethereal diazomethane solution (from 10 g. of nitrosomethylurea) was added and the reaction mixture was further kept in the cooling mixture for 24 hours. The ether–alcohol mixture was evaporated under reduced pressure (water-pump) and the solid residue redissolved in cold ether and washed twice with aqueous potassium hydroxide (25%). The ether was then thoroughly washed with water and dried (Na_2SO_4). The ether was then driven off and the solid residue washed several times with cold light petroleum (b. p. 40—60°). The insoluble residue melts at 120—122°. The petroleum extract was further concentrated and then, on cooling, was filtered from the separated crystals (m. p. 120—122°) and the mother-liquor was allowed to evaporate slowly, giving a crystalline residue, m. p. 80—110°. This crystalline residue was then washed several times with cold light petroleum (b. p. 40—60°) and the insoluble part (m. p. 120°) was removed. The last light petroleum extract was concentrated, whereupon crystals separated (m. p. 90—95°) which were further thrice

recrystallised from light petroleum (b. p. 40—60°), giving a small amount of colourless uniform crystals, m. p. 93—96°, enough for one micro-analysis (Found : C, 81·4; H, 9·2. Calc. for $C_{24}H_{32}O_2$: C, 81·8; H, 9·1%). A mixed m. p. with an authentic specimen gave no depression.

The analysis have been done by Dr. Weiler and Dr. Strauss, Oxford, and three concordant analysis of material obtained from three different experiments were obtained.

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[*Received, May 24th*, 1950.]

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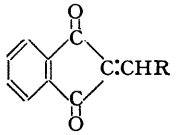
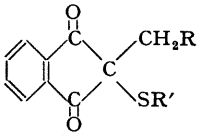
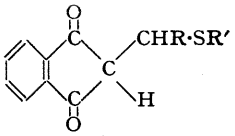
307. *The Addition of Thiols to 2-Arylmethylideneindane-1 : 3-diones.*

By AHMED MUSTAFA.

SINCE 2-arylmethylideneindane-1 : 3-diones (I) undergo addition reactions, *e.g.*, with malonic ester in the presence of piperidine (Ionescu, *Bull. Soc. chim.*, 1925, [iv], **37**, 913; *Bul. Soc. Stiinte Cluj*, 1926, **3**, 112), the addition of thiols to a series of such diones has been investigated. When yellow 2-benzylideneindane-1 : 3-dione (I; R = Ph) and thiophenol were heated together on the water-bath without a catalyst (cf. Nicolet, *J. Amer. Chem. Soc.*, 1935, **57**, 1098), addition occurred within five minutes, to give the colourless adduct (III; R = R′ = Ph). This regenerates thiophenol and (I) at the melting point or when heated with aqueous potassium hydroxide (cf. Nicolet, *ibid.*, 1931, **53**, 3066).


(I.)


(II.)


(III.)

The products obtained could be represented by either (II) or more probably (III) (cf. Nicolet, *loc. cit.*; Ruhemann, *J.*, 1905, 461). The latter structure accords with the fact that it (III;

2-[α-*Aryl*(*or benzyl*)*thio*-α-*arylmethyl*]*indane*-1 : 3-*diones* (III).

				Found, %,				Required, %,			
R.	R′.	M. p.*	Formula.	C.	H.	N.	S.	C.	H.	N.	S.
Ph	Ph	89—90°	$C_{22}H_{16}O_2S$	76·6	4·5	—	9·1	76·8	4·6	—	9·3
Ph	*o*-Tolyl	113	$C_{23}H_{18}O_2S$	77·1	4·9	—	8·7				
Ph	*p*-Tolyl	102	,,	76·9	5·1	—	8·8	77·1	5·0	—	8·95
Ph	Benzyl	89—90	,,	77·0	4·8	—	8·6				
m-Tolyl	Ph	97—98	,,	77·0	4·9	—	8·9				
m-Tolyl	*p*-Tolyl	100—101	$C_{24}H_{20}O_2S$	77·2	5·3	—	8·4	77·4	5·4	—	8·6
p-Tolyl	Ph	84	$C_{23}H_{18}O_2S$	76·8	4·8	—	8·6	77·1	5·0	—	8·95
p-Tolyl	*o*-Tolyl	82	$C_{24}H_{20}O_2S$	77·1	5·2	—	8·3				
p-Tolyl	*p*-Tolyl	110	,,	77·4	5·1	—	8·5	77·4	5·4	—	8·6
p-Tolyl	Benzyl	76	,,	77·2	5·0	—	8·3				
o-NO_2·C_6H_4	Ph	120	$C_{22}H_{15}O_4NS$	67·5	3·7	3·6	8·1	67·8	3·9	3·6	8·2
o-NO_2·C_6H_4	*o*-Tolyl	115	$C_{23}H_{17}O_4NS$	68·3	4·0	3·1	7·6				
o-NO_2·C_6H_4	*p*-Tolyl	109	,,	68·4	4·1	3·0	7·8	68·5	4·2	3·4	7·9
o-NO_2·C_6H_4	Benzyl	111—112	,,	68·3	4·2	3·2	7·6				
m-NO_2·C_6H_4	Ph	120	$C_{22}H_{15}O_4NS$	67·6	3·7	3·4	7·9	67·8	3·9	3·6	8·2
m-NO_2·C_6H_4	*o*-Tolyl	82	$C_{23}H_{17}O_4NS$	68·4	4·1	3·0	7·7				
m-NO_2·C_6H_4	*p*-Tolyl	120	,,	68·1	4·2	3·3	7·5	68·5	4·2	3·4	7·9
m-NO_2·C_6H_4	Benzyl	99	,,	68·2	3·9	3·0	7·8				
p-NO_2·C_6H_4	Ph	118	$C_{22}H_{15}O_4NS$	67·5	3·6	3·5	8·0	67·8	3·9	3·6	8·2
p-NO_2·C_6H_4	*o*-Tolyl	119	$C_{23}H_{17}O_4NS$	68·2	4·0	3·1	7·5				
p-NO_2·C_6H_4	*p*-Tolyl	131	,,	68·1	4·1	3·0	7·4	68·5	4·2	3·4	7·9
p-NO_2·C_6H_4	Benzyl	139	,,	68·0	4·0	3·4	7·6				
p-C_6H_4Cl	Ph	110	$C_{22}H_{15}O_2ClS$ [1]	69·4	3·6	—	8·0	69·7	3·9	—	8·4
p-C_6H_4Cl	*o*-Tolyl	108	$C_{23}H_{17}O_2ClS$ [2a]	69·9	4·0	—	7·8				
p-C_6H_4Cl	*p*-Tolyl	111	,, [2b]	70·1	4·1	—	8·1	70·3	4·3	—	8·1
p-C_6H_4Cl	Benzyl	83	,, [2c]	69·9	3·9	—	8·0				

* With decomp. [1] Found : Cl, 8·9. Reqd. : Cl, 9·4%. [2] Found : Cl (*a*) 7·8, (*b*) 8·1, (*c*) 8·0. Reqd. : Cl, 9·0%.

The compounds were recrystallised from light petroleum (b. p. 40—60°). In cold, concentrated sulphuric acid they give deep green solutions, which when heated on the water-bath develop the colour acquired by the corresponding 2-arylmethylideneindane-1 : 3-dione when the latter is treated with cold sulphuric acid. They are colourless, except that the nitro-compounds are very pale yellow.

R = R′ = Ph) dissolves in cold, aqueous ammonia with an orange-red colour (owing to enolisation; cf. the purplish-red colour of 1 : 2-diphenylindenone); neutralisation with ice-cold, dilute hydrochloric acid liberates (III; R = R′ = Ph).

o- and *p*-Thiocresol and toluene-ω-thiol give similar adducts (cf. Table).

EXPERIMENTAL.—*Addition of thiols to 2-arylmethylideneindane-1 : 3-diones.* Equimolecular quantities of the reactants were heated for 5 minutes on the steam-bath, a clear solution being obtained. The solution was shaken quickly with excess of light petroleum (b. p. 40—60°) and filtered. On cooling, the filtrate gave an almost quantitative yield of the adduct.

Thermal decomposition. The adduct (1 g.), *e.g.*, (III; R = R′ = Ph), was heated in an oil-bath (bath-temp., 120°) in a stream of dry carbon dioxide for 20 minutes. The cooled melt was extracted with light petroleum (b. p. 30—50°), the extract was evaporated, and the oily residue treated with benzoyl chloride in the presence of sodium hydroxide; colourless crystals were obtained which, after recrystallisation from ethyl alcohol, proved to be phenyl thiolbenzoate (m. p. and mixed m. p.) (Found : C, 72·6; H, 4·9; S, 14·9. Calc. for $C_{13}H_{10}OS$: C, 72·9; H, 4·7; S, 14·9%). The part insoluble in light petroleum was crystallised from benzene in yellow crystals, m. p. 151°, and proved to be 2-benzylideneindane-1 : 3-dione (m. p. and mixed m. p., and colour reaction with sulphuric acid).

When the addition compounds obtained from *o*-thiocresol or toluene-ω-thiol were thermally decomposed, the thiols obtained were identified as the corresponding disulphides. *p*-Thiocresol was identified as its benzoyl derivative (m. p. and mixed m. p.).

Alkaline hydrolysis. To a solution of the adduct, *e.g.* (III; R = R′ = Ph), in alcohol (50 c.c.) was added 5% aqueous potassium hydroxide (10 c.c.), and the mixture heated on a boiling water-bath for 10 minutes. After cooling, it was neutralised with cold, dilute hydrochloric acid and extracted with ether, the extract being dried and evaporated. The oily residue was treated with light petroleum (b. p. 30—50°); the soluble part proved to be thiophenol (cf. above), and the insoluble part was the dione.

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308. *The Catalytic Hydrogenation of Diphenyl in the Presence of Raney Nickel.*

By ISAAC GOODMAN.

THE earliest studies of the catalytic hydrogenation of diphenyl were those by Eykman (*Chem. Weekblad.*, 1903, 7) and Sabatier and Murat (*Ann. Chim.*, 1915, **4**, 253). Eykman succeeded only in obtaining the hexahydro-compound, but the latter investigators prepared dodecahydrodiphenyl (di*cyclo*hexyl) by repeated passage of diphenyl vapour with hydrogen over a nickel catalyst. In a subsequent investigation by Kagehira (*Bull. Chem. Soc., Japan*, 1931, **6**, 241), di*cyclo*hexyl was obtained as the primary hydrogenation product at 80—200°, but at higher temperatures dehydrogenation (so-called " partial oxidation ") occurred, giving phenyl*cyclo*hexane. The platinum-oxide-catalysed hemihydrogenation of various compounds containing two benzene nuclei has been studied by Smith, Alderman, Shacklett, and Welch (*J. Amer. Chem. Soc.*, 1949, **71**, 3772) who found that, whilst diphenylmethane and *as*-diphenylethane could be uniquely converted into the phenyl*cyclo*hexyl analogues, diphenyl gave a mixed product containing only 60% of phenyl*cyclo*hexane. None of these methods offers a convenient procedure for the selective hydrogenation of diphenyl, and indeed the hemihydrogenation product has been more easily obtained by the *cyclo*hexylation of benzene, although considerable by-product formation occurs (*Org. Synth.*, Coll. Vol. **2**, p. 151). The catalytic hydrogenation, in suitable conditions, of diphenyl has now given phenyl*cyclo*hexane and di*cyclo*hexyl separately in good yield and substantially free from one another.

A study of the hydrogenation curves (pressure–time) in falling-pressure experiments indicated the occurrence at different temperatures of three distinct processes. Rapid hydrogenation to di*cyclo*hexyl occurred only at 200°, giving high yields. The other processes were the rapid partial hydrogenation to phenyl*cyclo*hexane, followed by the slower hydrogenation of this to di*cyclo*hexyl. At 160°, for example, the curve showed an initial rapid reaction upon which was superimposed the less rapid, but still considerable, rate of further hydrogenation.

These conditions were still not specific for the hemihydrogenation of diphenyl, and the reaction temperature was therefore reduced to 100°, and finally to 80°. When, in these conditions, the hydrogenation was allowed to proceed until no further absorption was observed, it was still found that some overhydrogenation (*i.e.* more than the 3 moles of hydrogen per mole

of diphenyl) had occurred; this excessive absorption appeared to occur in the relatively long period between the end of the first, rapid pressure drop and the complete cessation of absorption. Interruption of the reaction at the end of the first period, and distillation of the product, gave a high yield of phenyl*cyclo*hexane whose purity was established by comparison with a sample obtained by desulphonation of sodium *p-cyclo*hexylbenzenesulphonate.

It is interesting that hydrogenation of phenyl*cyclo*hexane occurs, albeit slowly, even at 80°. In the hydrogenation of fluorene, whose reactivity in many respects resembles that of diphenyl, it has not been found possible to interrupt the reaction at the hexahydro-stage, and perhydrogenation here appears even more prominent.*

*Experimental.—Preparation of di*cyclo*hexyl.* Diphenyl (100 g.), ethanol (80 c.c.), and Raney nickel (10 g.) were shaken in a stainless-steel autoclave with hydrogen [initial (cold) pressure, 1450 lbs./sq. in.]. Hydrogenation was continued for 15 hours at 200°, whereupon the pressure was steady. The product was freed from alcohol by distillation, and the di*cyclo*hexyl washed with concentrated sulphuric acid to remove any aromatic component. Distillation then gave di*cyclo*hexyl (100 g., 92·5%), b. p. 235—239°/767 mm., n_D^{20} 1·4849, $d_4^{23\cdot5}$ 0·885. The observed pressure drop in this experiment corresponded to 5·88 moles of hydrogen per mole of diphenyl (98%).

*Preparation of phenyl*cyclo*hexane.* Diphenyl (20 g.), ethanol (16 c.c.), and Raney nickel (4 g.) were shaken at 100° with hydrogen (initial pressure 900 lbs./sq. in. at 20°). The reaction was interrupted after 3½ hours; the observed pressure drop corresponded to an uptake of 2·89 moles of hydrogen per mole of diphenyl (96·4%). Distillation of the product gave phenyl*cyclo*hexane (18 g., 86·7%), b. p. 100—102°/15 mm., n_D^{20} 1·5217. Desulphonation of the sodium sulphonate gave a product, b. p. 103—105°/12 mm., n_D^{26} 1·5236.

Uninterrupted hydrogenation at 80° *and* 100°. Diphenyl was hydrogenated as in the previous experiment until no further pressure drop occurred. The products were distilled, and their compositions determined from the refractive indices. In all cases, formation of significant quantities of di*cyclo*hexyl had occurred.

			Product.		
Temp.	Reaction time, hrs.	Absorption.*	B. p.	n_D^{20}.	Di*cyclo*hexyl, %.
100°	11·5	3·23	99—108°/10 mm.	1·5157	20
100	8	3·2	230—236°/760 mm.	1·5142	23
80	8·5	3·17	93—100°/15 mm.	1·5152	21

* Moles of hydrogen per mole of diphenyl.

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309. *Phormium Gum.*

By R. J. MCILROY.

A PRELIMINARY examination (McIlroy, *N.Z.J. Sci. Tech.*, 1944, **26**, *B*, 161) of the gum exuded from the leaves of *Phormium tenax* indicated that it is a polysaccharide composed of D-glucuronic acid, a pentose, and possibly D-glucose. The aqueous solution of the gum was neutral, non-reducing, and lævorotatory ($[\alpha]_D^{14}$ −63°). The equivalent by titration was 880.

Proximate analysis of the purified gum by the usual methods indicated the following composition: uronic anhydride, 42·4 (carbon dioxide 10·6%); anhydropentose, 45·0 (furfuraldehyde 37·0%); apparent lignin, 3·8; ash, 5·0%.

The reducing sugar obtained on hydrolysis was converted quantitatively into dibenzylidene D-xylose dimethylacetal, m. p. and mixed m. p. 212° (Breddy and Jones, *J.*, 1945, 738; Wise and Ratliff, *Ind. Eng. Chem. Anal.*, 1947, **19**, 694). This indicates that D-xylose is the only sugar present; phormium gum is thus a polyuronide constituted of D-xylose and D-glucuronic acid residues, and is comparable to Phormium hemicellulose (McIlroy, Holmes, and Mauger, *J.*, 1945, 796; McIlroy, *J.*, 1949, 121).

On periodate oxidation the gum consumed 1·7 mols. of periodate per anhydroxylose unit, compared with xylan which consumed 1·2 mols. of periodate (Chanda, Hirst, Jones, and Percival, *J.*, 1950, 1296). The periodate consumption indicates a predominance of α-glycol residues in

* I am indebted to one of the Referees for drawing my attention to the work of Idris Jones and Lindsey (*J.*, 1950, 1836) on the Raney-nickel-catalysed hydrogenation at 200° of a dihydroxydiphenyl and diphenylene oxide. In both cases, hemireduction gave only limited yields of the hexahydro-compounds, together with hydrogenolysis products and unhydrogenated material. The two compounds are thus more resistant to controlled hydrogenation than are the hydrocarbon analogues.

the xylose chain, as in xylan. The greater consumption of periodate by the gum is, no doubt, due to the presence of uronic acid. A terminal residue of uronic acid consumes at least 2 mols. of periodate and possibly more on over-oxidation. These results are in agreement with either 1 : 2- or 1 : 4-linkages, although the latter, by analogy with xylan and hemicellulose, are more probable.

Phormium gum was extremely resistant to methylation and was degraded in the process. Methyl sulphate and sodium hydroxide in aqueous acetone (six treatments) followed by methyl iodide–silver oxide (three treatments) gave a product (OMe 28·6%; yield 6%). Attempts to prepare a more highly methylated gum by the thallous hydroxide–methyl iodide method were unsuccessful.

Experimental.—Purification of the gum. The crude gum collected from *Phormium tenax* var. S.S., grown on the Moutoa Estate, Foxton, N.Z., was dissolved in hot water, and the hot solution filtered through glass wool. Addition of an equal volume of 95% alcohol to the cooled solution, after acidification with glacial acetic acid, precipitated the gum as a colourless, ropy coagulum which was separated by vacuum filtration on cloth and washed free from acid. The viscous crude gum (642 g.) yielded 63 g. of dried, purified product (ash, 5·0%).

Estimation of uronic anhydride. The purified gum (10 mg.) was heated with 12% hydrochloric acid saturated with sodium chloride for 3·5 hours at 135—137° (bath temp.) (Burkhart, Baur, and Link, *J. Biol. Chem.*, 1934, **104**, 171). 10·6% of carbon dioxide, corresponding to 42·4% (10·6 × 4) of uronic anhydride was produced.

Estimation of xylose. The purified gum (1·02 g.; ash, 5·6%) was hydrolysed with 3% sulphuric acid for 21 hours at 100° {final rotation, $[\alpha]_D^{12}$ +50° (c = 1)}. The solution, neutralised by barium carbonate, was evaporated to dryness and the free sugars extracted with boiling alcohol. The material (0·39 g.) obtained on evaporation of the extracts was treated with Breddy and Jones's reagent (*loc. cit.*), and gave a quantitative yield of dibenzylidene xylose dimethylacetal, m. p. and mixed m. p. 212°, indicating that xylose is the only sugar present.

Heating of the gum with 18·5% hydrochloric acid gave furfuraldehyde (37%; 72·8% phloroglucide precipitate), a portion of which is derived from uronic anhydride. Uronic anhydride yields 21·48% of furfuraldehyde under these conditions. The anhydroxylose content (45·0%) was calculated by use of Angell, Norris, and Resch's formula (*Biochem. J.*, 1936, **30**, 2146).

Periodate oxidation. Duplicate samples of dry, purified gum (200 mg.) (ash 5%) in water (20 c.c.) were oxidised (Halsall, Hirst, and Jones, *J.*, 1947, 1430; Jeanes and Wilham, *J. Amer. Chem. Soc.*, 1950, **72**, 2657) with an excess of sodium metaperiodate (25 c.c.; 0·298M.) at 25°. The amount of periodate consumed (mols. per $C_5H_8O_4$ unit) was determined by Fleury and Lange's method (*J. Pharm. Chim.*, 1933, **17**, 107, 196): 1·75 (50 hrs.); 1·72 (74 hrs.); 1·80 (100 hrs.). A sample (198·4 mg.) of esparto xylan oxidised under identical conditions at the same time consumed periodate (mols. per $C_5H_8O_4$ unit): 1·20 (50 hrs.); 1·21 (74 hrs.); 1·21 (100 hrs.). These results are in close agreement with those obtained for esparto xylan by Chanda, Hirst, Jones, and Percival (*loc. cit.*).

UNIVERSITY COLLEGE, IBADAN, NIGERIA. [*Received, January 17th*, 1951.]

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310. *The Dehydrogenation of* 1 : 2 : 3 : 4-*Tetrahydrocarbazole.*

By W. E. BADCOCK and K. H. PAUSACKER.

1 : 2 : 3 : 4-TETRAHYDROCARBAZOLE has been dehydrogenated, forming carbazole, by (*a*) distillation over lead oxide (Borsche, Witte, and Bothe, *Annalen*, 1908, **359**, 74), (*b*) sulphur in boiling quinoline (Perkin and Plant, *J.*, 1923, **123**, 694), (*c*) palladised charcoal in a stream of hydrogen at *ca.* 300° (Pausacker and Schubert, *J.*, 1949, 1387), (*d*) palladised charcoal in boiling xylene (Horning, Horning, and Walker, *J. Amer. Chem. Soc.*, 1948, **70**, 3935), (*e*) fusion with palladium and cinnamic acid (Hoshino and Takiura, *Bull. Chem. Soc. Japan*, 1936, **11**, 218), and (*f*) chloranil in boiling xylene (Barclay and Campbell, *J.*, 1945, 530).

It has now been found that when a xylene solution is refluxed in the presence of Raney nickel, carbazole is formed in theoretical yield along with the evolution of almost two moles of hydrogen. Light petroleum (b. p. 100—120° or 70—90°) may also be used as a solvent, but the yields were lower (91 and 52% respectively). When *cyclo*hexanone was added, carbazole was again obtained in theoretical yield, *cyclo*hexanol (30% yield, isolated as its 3 : 5-dinitrobenzoate) also being formed. Kleiderer and Kornfeld (*J. Org. Chem.*, 1948, **13**, 455) have also used this method for oxidising alcohols to carbonyl compounds. However, the presence of hydrogen acceptors, other than *cyclo*hexanone, caused a decrease in yield. Thus, under the same conditions, the acceptors and yields are: phenyl*cyclo*hexene (73%), benzophenone (65%), fluorenone (59%), and cinnamic acid (31%).

The method does not appear to be general, as 3-chloro- and 3-nitro-carbazole could not be isolated when 6-chloro-1 : 2 : 3 : 4-tetrahydro- and 1 : 2 : 3 : 4-tetrahydro-6-nitro-carbazole were treated with Raney nickel in xylene. In addition, it was found that tetralin was converted

into naphthalene (isolated as its picrate, 13%), although decalin is unchanged (cf. Paul, *Bull. Soc. chim.*, 1940, **7**, 334).

Experimental.—Sulphur-free xylene (60 ml.) was added to Raney nickel (5 ml.), and 10 ml. were distilled off to remove any alcohol. 1 : 2 : 3 : 4-Tetrahydrocarbazole (4·3 g.) was added and the mixture refluxed for 6 hours. After filtration of the hot solution, the xylene was removed *in vacuo* and the residue sublimed, yielding carbazole (4·2 g.; m. p. 235°).

Quantitative runs were performed by first boiling the alcohol-free Raney nickel in xylene until hydrogen evolution ceased and then adding the compound to be dehydrogenated. The following results were obtained, the figures in parentheses representing the wt. of substance (g.), volume of hydrogen (ml.), and percentage of theoretical volume: tetrahydrocarbazole (3·8, 1140, 96); 6-chloro-1 : 2 : 3 : 4-tetrahydro- (3·0, 80, 18) and 1 : 2 : 3 : 4-tetrahydro-6-nitro-carbazole (3·0, 40, 6·2); 1 : 2 : 3 : 4-tetrahydro-11-methylcarbazolenine (3·0, 74, 17); and tetralin (1·9, 250, 45). The rate of evolution of hydrogen from tetrahydrocarbazole appeared to follow a first-order sequence ($k = 5 \times 10^{-4}$ sec.$^{-1}$).

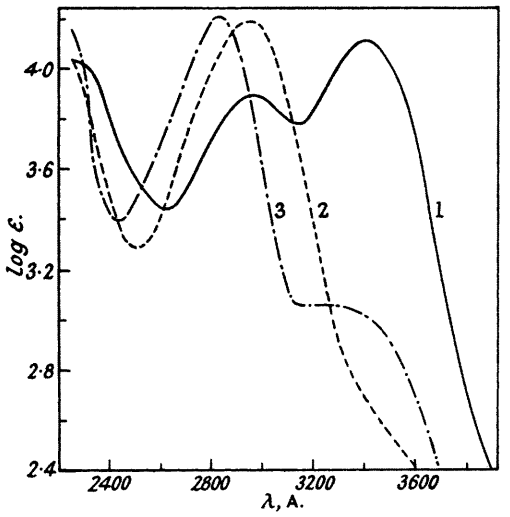
UNIVERSITY OF MELBOURNE, N.3, VICTORIA, AUSTRALIA. [*Received, January 18th*, 1951.]

311. *The Structure of 4-Pyridthione.*

By I. G. Ross.

CHEMICAL and physical measurements, especially those by Specker and Gawrosch (*Ber.*, 1942, *B*, **75**, 1338), on the compound obtained by inserting a hydroxyl group in the 4-position of pyridine have shown that it is undoubtedly to be formulated as 4-pyridone (I; X = O). No corresponding examination has been recorded of its sulphur analogue, which may be either 4-pyridthione (I; X = S), pyridine-4-thiol (IV; X = S), or a tautomeric mixture of both.

The sulphur analogue is a pale yellow solid, freely soluble in hydroxylic solvents, giving a yellow solution which is decolorised by the addition of either acid or alkali. The absorption spectra in various media have now been measured, and details are given in the figure and the table; in the latter f is the oscillator strength, calculated from the formula, $f = 4{\cdot}31 \times 10^{-9} \int \varepsilon d\nu$, where ν is the frequency in cm.$^{-1}$.



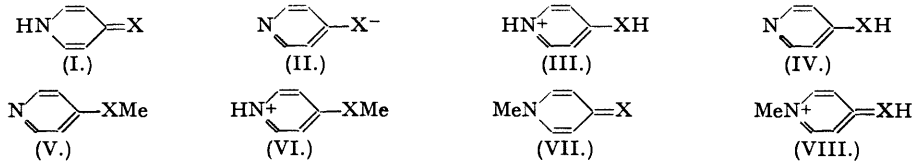
Spectra of 4-pyridthione. 1. *In ethanol.* 2. *In* 0·1N-*ethanolic ammonia.* 3. *In* 0·1N-*ethanolic hydrogen chloride.*

The discussion of these spectra must be made in conjunction with those of 4-pyridone, and the spectra of this compound have therefore been measured in the same media; the data obtained are included in the table, but the curves themselves differ so little (apart from a small wave-length shift) from those obtained in methanol solution by Specker and Gawrosch (*loc. cit.*) that their separate presentation is unnecessary. The table lists the principal band systems observed, together with their tentative assignments to the various molecular and ionic species whose existence in the solution must be considered; the assignments for pyridone and its derivatives are those by Specker and Gawrosch, except for (VIII), the nature of the band concerned having been left an open question by these authors.

The fact that the absorption of quinonoid 4-pyridone (I) does not resemble that of *p*-benzoquinone is in keeping with the fact that *p*-benzoquinoneimine is also colourless; the 3410-A. band in 4-pyridthione is also attributed to a quinonoid structure, the frequency shift (−9740 cm.$^{-1}$) being in keeping with the quasi-classical theory of light absorption advanced by Lewis and Calvin (*Chem. Reviews*, 1939, **25**, 273). An alternative possibility, that it is due to a singlet–triplet transition, localised within the C:S group, such as occurs in diphenylthione (Lewis and Kasha, *J. Amer. Chem. Soc.*, 1945, **67**, 994), may be discounted by applying Lewis and Kasha's criteria for such bands; in particular, the wave-length is rather too short, and the intensity, for a spin-forbidden transition, far too great.

Albert and Short (*J.*, 1945, 760) have observed that 2- and 4-acridone exist in the tautomeric hydroxy-forms in solvents of low dielectric constant; it might be expected that, similarly, the

benzenoid form (IV) of pyridthione could be detected in hexane solution. The substance is, however, almost insoluble in *n*-hexane. Nevertheless, a saturated solution (2 cm. path) did show an unmistakable band at 2350 A. (maximum extinction 0·22), together with about 2% absorption between 2700 and 3300 A. This band has no parallel in the spectra shown in the figure, and may well be attributable to (IV); it must then be regarded as shifting to 2600 A. on *S*-methylation (V; X = S). It may be noted that a large shift also occurs on *S*-methylation of thiophenol (2360 to 2540 A.) (Koch, *J.*, 1949, 391; Fehnel and Carmack, *J. Amer. Chem. Soc.*, 1949, **71**, 84). A comparable band could not be observed in 4-pyridone, a saturated *n*-hexane solution of which shows no measurable absorption at wave-lengths down to 2200 A.



Absorption bands of 4-pyridone and 4-pyridthione.

	X = O.				X = S.			
Solute.	Solvent.	$\lambda_{max.}$.	log $\varepsilon_{max.}$.	*f.*	Solvent.	$\lambda_{max.}$.	log $\varepsilon_{max.}$.	*f.*
(I)	EtOH	2560	4·16	0·26	EtOH	3410	(4·11)	(0·19)
(II)	EtOH + NaOEt	2430	4·05	0·22	EtOH + NH_3	2950	4·18	0·28
		2600*S*	3·85					
(III)	EtOH + HCl	2350	3·99	0·18	EtOH + HCl	2825	4·20	0·26
(IV)	—	—	—	—	C_6H_{14}	2350	—	—
(V)	MeOH [a]	2180	3·9	—	EtOH [b]	2600	4·2	—
		2450*S*	3·0	—				
(VI)	MeOH + HCl [a]	2400	4·1	—				
(VII)	MeOH [a]	2600	4·2	—				
(VIII)	MeOH + HCl [a]	2370	4·0	—				

(*a*) Specker and Gawrosch, *loc. cit.*; (*b*) Welsh, unpublished measurement (Thesis, Sydney, 1946). *S* denotes an unresolved shoulder.

Experimental.—4-Pyridone and 4-pyridthione were prepared by King and Ware's methods (*J.*, 1939, 873); 4-pyridone was vacuum-distilled, and obtained as lustrous plates, m. p. 149°, after two crystallisations from acetone (charcoal); 4-pyridthione was recrystallised several times from methanol containing a little ethanol (charcoal), and then had m. p. 184°.

The absorption spectra were measured with a Cary recording spectrophotometer.

I am indebted to Mr. A. Boden, Hardman Research Laboratory, Sydney, for a gift of chemicals; to Mr. F. Walker for carrying out some of the preparative work; and to Dr. D. P. Craig for discussions on this work, which was carried out during the tenure of an Australian National University Scholarship.

William Ramsay and Ralph Forster Laboratories,
University College, London, W.C.1. [*Received, January* 31*st*, 1951.]

312. *The Preparation of* 1-*Bromo*-2-*methylnaphthalene.*

By D. Muriel Hall and R. K. Mitchell.

1-Bromo-2-methylnaphthalene has been obtained by monobromination of 2-methylnaphthalene in carbon disulphide by Schulze (*Ber.*, 1884, **17**, 1527), Mayer and Sieglitz (*Ber.*, 1922, **55**, 1835; 70% yield; b. p. 165—170°/13 mm.), and others (*e.g.*, Fuson, McKeever, and Behr, *J. Amer. Chem. Soc.*, 1941, **63**, 2648; 92% yield; b. p. 125—129°/5 mm.). Adams and Binder (*J. Amer. Chem. Soc.*, 1941, **63**, 2773) used carbon tetrachloride as solvent, with iodine and iron powder as catalysts and with the exclusion of light; they added the bromine (160 g.) in carbon tetrachloride solution during 8 hours, with mechanical stirring and at $\gtrsim$5°; they obtained an 84% yield and b. p. 152—156°/14 mm.

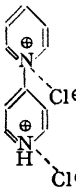
We now find that, by using the quantities and conditions of Adams and Binder (*loc. cit.*) but adding the bromine solution during 15 minutes and continuing the stirring for a further 40 minutes before adding aqueous sodium hydroxide, we obtain an 87% yield and b. p. 112—117°/1 mm. From 142 g. of 2-methylnaphthalene the average yield from five preparations is 193 g. (87%).

Bedford College, London. [*Received, February* 2*nd*, 1951.]

313. 4-*Aminopyridine.*

By Adrien Albert.

It has been claimed that 4-aminopyridine can be prepared in 60% yield by heating 1-4′-pyridylpyridinium chloride hydrochloride (I) with aqueous ammonia at 150° (Koenigs and Greiner, *Ber.*, 1931, **64**, 1052). Experience has shown that this reaction often fails and for this reason it has been suggested by Mosher (Elderfield's " Heterocyclic Compounds," 1950, Vol. I, p. 552, Wiley, New York) that 4-aminopyridine should preferably be prepared from 4-picoline *via* the Curtius or Hofmann degradation of pyridine-4-carboxylic acid.



(I.)

However it was found possible to obtain a repeatable yield of 80% of 4-aminopyridine from (I) by the use of ammonia, in the presence of phenol, in an open vessel. This approach was suggested by many previous successful experiences in the amination of γ-chloro-groups by this method in the acridine, benzacridine, quinoline, benzoquinoline, and phenanthroline series (Albert, Brown, and Duewell, *J.*, 1948, 1284; Albert and Gledhill, *J. Soc. Chem. Ind.*, 1945, **64**, 169). Because (I) is available commercially (it can also be readily prepared in the laboratory from pyridine and thionyl chloride) this one-stage method offers a distinct advantage over the suggested preparation from 4-picoline which is not readily obtained pure.

Experimental.—The salt (I) was prepared by Koenigs and Greiner's method (*loc. cit.*) and purified by dissolving each gram in 0·5 ml. of boiling 0·1N-hydrochloric acid, filtration from colloidal material, treatment with charcoal, re-filtration, and evaporating to crystallizing point. This hot solution was diluted with an equal volume of absolute alcohol and kept at −4° for a day; then the white crystals were filtered off (80% recovery; m. p. 171—173°). The yield was 50% based on pyridine taken.

Purified (I) (14·6 g.) and phenol (58·5 g.) were heated under reflux in a bath at 180—190° while ammonia was passed at 2—3 bubbles per second for 3 hours. The method of isolation was devised from knowledge that 4-aminopyridine is highly hydrophilic and a strong base (pK_a 9·2). The partition coefficient between chloroform and water was found to be about 0·2, and the solubility in chloroform at 20° was about 1 in 40 (about 1 in 20 at the boil) and in water at 20° it was about 1 in 12.

The flask was cooled, water (20 ml.) added, and the pH adjusted to 7 with a little N-hydrochloric acid. The contents were then distilled in steam (to remove phenol), readjusted to pH 7 with a little 10N-sodium hydroxide, and evaporated to a paste which was stirred with 10N-sodium hydroxide (about 10 ml. or enough to redden Tropaeolin OOO, *i.e.*, pH *ca.* 12). The mixture was filtered through a No. 54 Whatman paper. The filter-cake was well pressed, then transferred to porous tile to drain, while the filtrate was extracted with chloroform (75 + 75 + 75 ml.). The filter-cake was then extracted with boiling chloroform (120 + 100 + 50 ml.). The combined extracts were concentrated to 10 ml., giving 4·8 g. (80%) of 4-aminopyridine, m. p. 155—158°. Recrystallization, by continuous extraction with benzene (50 ml.), gave white crystals (90% recovery), m. p. 158°, which is the highest melting point recorded.

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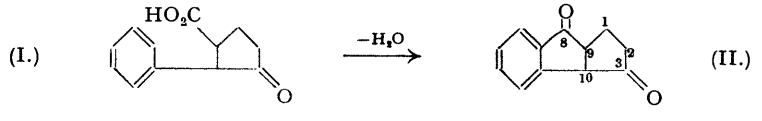
314. *Fluorosulphonic Acid as a Cyclodehydrating Agent.*

By Wilson Baker, G. E. Coates, and F. Glockling.

Unsuccessful attempts to effect the cyclisation of 3-keto-2-phenyl*cyclo*pentane-1-carboxylic acid (I) to 1 : 2 : 3 : 8 : 9 : 10-hexahydro-3 : 8-diketo*cyclo*pent[*a*]indene (II) (Baker and Jones, *J.*, 1951, 789) by a variety of standard methods, including the use of polyphosphoric acid (see Baker and Leeds, *J.*, 1948, 974; Snyder and Werber, *J. Amer. Chem. Soc.*, 1950, **72**, 2962, 2965), led us to investigate the possibility of using fluorosulphonic acid, $F{\cdot}SO_2{\cdot}OH$, for this purpose. It was found that fluorosulphonic acid reacted smoothly with (I) at room temperature, giving the desired diketone (II) in high yield. Details of this experiment will be reported later.



(I.) (II.)

In view of this successful reaction, fluorosulphonic acid, which is now commercially available, was used to effect the cyclodehydration of several aromatic acids to cyclic ketones. The results, tabulated below, show that very satisfactory yields of the ketones were obtained. β-Phenylpropionic acid gave, in addition to indan-1-one, a small quantity of the dimeric anhydroderivative, 2-1′-indanylideneindan-1-one. δ-Phenylvaleric acid gave no 1 : 2-benzo*cyclo*hepten-

3-one (benzsuberone) under the conditions employed, and extensive fluorosulphonation occurred. As a cyclodehydrating agent, fluorosulphonic acid has the advantage over hydrogen fluoride in that the reactions may be carried out in glass apparatus, although slight etching does occur. It is, moreover, less prone to form tarry by-products than some other cyclising agents. For a successful cyclisation, however, the conditions must be sufficiently vigorous to bring about cyclodehydration, but not such as will cause fluorosulphonation or sulphonation of either the starting material or the cyclic ketone. As the aromatic nucleus of the cyclic ketone is partly deactivated by the ketonic group, substitution is less likely to occur than in the original acid. For the same reason cyclisation of the acid is unlikely to occur if it has undergone previous fluorosulphonation or sulphonation, and it is therefore improbable that fluorosulphonic acid can be used for the cyclisation of acids possessing reactive aromatic nuclei, *e.g.* if they contain methoxyl or substituted amino-groups. The optimum conditions for cyclodehydration with fluorosulphonic acid require study in each particular case, and this reagent is likely to prove of greatest use where other methods of cyclisation fail, *e.g.* in the conversion of (I) into (II).

Acid.	Temp.	Time (hrs.).	Product.	Yield (%).
β-Phenylpropionic	100°	1½	Indan-1-one	68
γ-Phenylbutyric	15	5	α-Tetralone	61
Phenylsuccinic	100	1½	3-Ketoindane-1-carboxylic acid	77
o-Benzoylbenzoic	100	3	Anthraquinone	86

Fluorosulphonic acid has previously been used as a catalyst and as a fluorosulphonating or sulphonating agent (Steinkopf, *J. pr. Chem.*, 1927, **117**, 1; Langer and Müller, *Ber.*, 1930, **63**, 2653; Renoll, *J. Amer. Chem. Soc.*, 1942, **64**, 1489; Simons, Passino, and Archer, *ibid.*, 1941, **63**, 608), and its esters have also been investigated (Meyer and Schramm, *Z. anorg. Chem.*, 1932, **206**, 24). Adipic, suberic, and benzoic acids were unaffected by fluorosulphonic acid at room temperature; the first and last were also unchanged at 100°. Phenylacetic acid gave *p*-fluorosulphonylphenylacetic acid in high yield.

Experimental.—Indane-1-one and 2-1′-Indanylideneindan-1-one. β-Phenylpropionic acid (15 g.) and fluorosulphonic acid (16 c.c.) were heated on the steam-bath for 1½ hours, cooled, and poured into water, and the orange-brown oil extracted into ether. The ethereal extract, after addition of aqueous sodium carbonate, was steam-distilled and the distillate yielded pure indan-1-one (8·9 g.), m. p. 42° (lit., m. p. 39—41°). The cooled alkaline solution was filtered, giving 2-1′-indanylideneindan-1-one (0·35 g.) as pale yellow needles, m. p. 145°. Kipping (*J.*, 1894, **65**, 495) records m. p. 142—143° (Found, in material crystallised three times from ethanol: C, 88·1; H, 5·9. Calc. for $C_{18}H_{14}O$: C, 87·8; H, 5·7%). Acidification of the alkaline solution gave a trace of β-phenylpropionic acid.

α-Tetralone. γ-Phenylbutyric acid (10 g.) and fluorosulphonic acid (25 c.c.) were kept at room temperature for 5 hours, and the product was isolated as in the previous case, giving α-tetralone (5·4 g.), b. p. 79°/0·3 mm. The 2 : 4-dinitrophenylhydrazone had m. p. 255° (lit., m. p. 257°).

3-Ketoindane-1-carboxylic acid. Phenylsuccinic acid (12·8 g.) and fluorosulphonic acid (28 c.c.) were heated on the steam-bath for 1½ hours. The cooled mixture was poured into water (400 c.c.), heated to boiling, and treated with charcoal. The hydrated 3-ketoindane-1-carboxylic acid, m. p. 84°, which separated, was collected and dehydrated *in vacuo*, whereafter it had m. p. 118—119° (Baker and Leeds, *J.*, 1948, 980, record m. p. 120°).

Anthraquinone. *o*-Benzoylbenzoic acid (8·7 g.) and fluorosulphonic acid (25 c.c.) were heated on the steam-bath for 3 hours, cooled, poured into water, and the solid collected and dried (7·35 g.). Crystallisation from benzene gave anthraquinone (6·9 g.), m. p. and mixed m. p. 278°.

Reaction between δ-phenylvaleric acid and fluorosulphonic acid. δ-Phenylvaleric acid (0·50 g.) and fluorosulphonic acid (3 c.c.) were mixed with cooling and after 4 hours the mixture was poured into water and extracted with ether. The ether yielded colourless needles (0·57 g.) of *δ-p-fluorosulphonylphenylvaleric acid.* After two crystallisations from benzene–light petroleum (b. p. 60—80°) it had m. p. 129—130° (Found: C, 50·5; H, 5·0. $C_{11}H_{13}O_4FS$ requires C, 50·7; H, 5·0%). The *amide*, prepared by reaction with strong aqueous ammonia, separated from water in colourless plates, m. p. 142—144° (Found: C, 50·9; H, 5·6; N, 5·5; S, 12·5. $C_{11}H_{15}O_4NS$ requires C, 51·4; H, 5·8; N, 5·4; S, 12·4%).

p-Fluorosulphonylphenylacetic acid. Phenylacetic acid (15 g.) and fluorosulphonic acid (40 c.c.) were heated at 100° for 6 hours. After the mixture had been cooled and poured into water the solid was collected, washed with cold water, and dried (yield, 11·5 g.). Crystallisation first from benzene and then from water (charcoal) gave p-*fluorosulphonylphenylacetic acid* as colourless needles, m. p. 140° (Found: C, 44·0; H, 3·2. $C_8H_7O_4FS$ requires C, 44·1; H, 3·2%). The *amide*, prepared by reaction with strong aqueous ammonia, separated from water in colourless plates, m. p. 182° (Stewart, *J.*, 1922, **121**, 2561, records m. p. 176°; the specimen was not analysed) (Found: C, 45·0; H, 4·2; N, 6·8; S, 15·4. $C_8H_9O_4NS$ requires C, 44·7; H, 4·2; N, 6·5; S, 14·9%).

The authors are grateful to the Department of Scientific and Industrial Research for a grant (awarded to F. G.), and to the Imperial Smelting Corporation, Limited, Avonmouth, for a gift of fluorosulphonic acid.

THE UNIVERSITY, BRISTOL. [*Received, February 16th*, 1951.]

315. *Sulphonium Derivatives of* DL-*Methionine and* 5-(2-*Methylthioethyl*)*hydantoin.*

By R. O. Atkinson and F. Poppelsdorf.

Toennies and Kolb (*J. Amer. Chem. Soc.*, 1945, **67**, 849) prepared a few methylsulphonium halides from methionine, and studied some of the factors governing their formation. They carried out the reactions in formic acid containing varying, but small, amounts of acetic acid and water, and concluded that the reaction is increasingly favoured in the order of increasing dielectric constant of the medium (cf. Bost and Everett, *ibid.*, 1940, **62**, 1752). They prepared methionine-methylsulphonium iodide (I) and bromide, but failed to obtain the chloride in a crystalline form.

(I.) $[R{\cdot}SMe_2]^+I^-$ $[R{\cdot}SMe_2]^+MeSO_4^-$ (II.)

$R = HO_2C{\cdot}CH(NH_2){\cdot}CH_2{\cdot}CH_2{-}$ or $NH{\cdot}CO{\cdot}CH{\cdot}CH_2{\cdot}CH_2{-}$ (ring closed by CO——NH)

Recently we found that some sulphonium salts from methionine and 5-(2-methylthioethyl)-hydantoin were formed rapidly in a solely aqueous medium. Methionine-methylsulphonium iodide was prepared in 75% yield after only 6 hours at 45°, compared with 3 days at 25° in the formic–acetic acid–water medium used by Toennies *et al.* (*loc. cit.*). Methyl sulphate reacts vigorously with methionine and 5-(2-methylthioethyl)hydantoin to form the methosulphates (II) in 15 minutes in 54% and 80% yield respectively. These compounds are neutral, non-hygroscopic, and extremely soluble in water.

A procedure is described for converting the methionine methosulphate into the chloride.

Experimental.—5-(2-*Methylthioethyl*)*hydantoin.* Methionine (17·4 g.), sodium cyanate (17·4 g.), and water (100 c.c.) were refluxed until the solid had dissolved. Concentrated hydrochloric acid (240 c.c.) was added and heating continued for 30 minutes. The clear colourless solution was cooled to 0° overnight. The resulting solid was filtered off, recrystallised from water, and dried at 60° *in vacuo*. The yield was 16·2 g. (80%) and the m. p. 104—105° (Found: N, 16·1. Calc. for $C_6H_{10}O_2N_2S$: N, 16·2%).

Methionine-methylsulphonium iodide. Methionine (7·45 g., 0·05 mole), water (40 c.c.), and methyl iodide (7·8 g., 0·055 mole) were heated together for 6 hours at 45°. The clear solution was concentrated *in vacuo* to a thick syrup and this was triturated with hot ethanol. The salt was filtered off and recrystallised from aqueous alcohol, to give white crystals (10·4 g., 75%), m. p. 150° (decomp.) (Found: C, 24·7; H, 4·9; N, 4·7; S, 10·8; I^-, 44·0. Calc. for $C_6H_{14}O_2NSI$: C, 24·7; H, 4·8; N, 4·8; S, 10·9; I^-, 43·6%).

Methionine-ethylsulphonium iodide. Methionine (7·4 g.), water (40 c.c.), and ethyl iodide (8·6 g.) reacted as above to give the *iodide* (11·0 g., 71%), m. p. 161—162° (decomp.) (Found: C, 27·9; H, 5·1; N, 4·5; S, 10·5; I^-, 41·9. $C_7H_{16}O_2NSI$ requires C, 27·5; H, 5·2; N, 4·6; S, 10·5; I^-, 41·6%).

5-(2-*Methylthioethyl*)*hydantoin-methylsulphonium iodide.* The hydantoin (8·7 g.), water (40 c.c.), and methyl iodide (7·8 g.) reacted as above to give the *iodide* (12·8 g., 86·5%), m. p. 175° (decomp.) (Found: C, 27·9; H, 3·8; N, 9·5; S, 10·9; I^-, 42·7. $C_7H_{13}O_2N_2SI$ requires C, 28·2; H, 3·7; N, 9·4; S, 10·8; I^-, 42·9%).

Methionine-methylsulphonium (*methyl sulphate*). Methionine (7·45 g.) was mixed with water (10 c.c.), and methyl sulphate (6·6 g.) was added. The mixture was warmed for a few minutes on a steam-bath with occasional agitation, whereupon the pasty mass became liquid and a vigorous exothermic reaction set in. Water-cooling was used to keep the temperature below 80°. The reaction finished in 15 minutes and the product was cooled to room temperature. Ethanol (250 c.c.) was added with rapid stirring, and the precipitated *methosulphate* was filtered off and recrystallised from aqueous alcohol, the yield being 7·4 g. (54%) and the m. p. 145° (decomp.). A test for sulphate ions was negative until after hydrolysis (Found: C, 30·9; H, 5·7; N, 5·2; S, 23·7; SO_4^{2-}, 32·9. $C_7H_{17}O_6NS_2$ requires C, 30·6; H, 6·2; N, 5·1; S, 23·3; SO_4^{2-}, 34·9%).

5-(2-*Methylthioethyl*)*hydantoin-methylsulphonium* (*methyl sulphate*). The hydantoin (8·7 g.), water (25 c.c.), and methyl sulphate (6·6 g.) were treated as above to give the *product* (12·0 g., 80%), m. p. 168° (decomp.) (Found: C, 32·3; H, 5·3; N, 9·3; S, 21·7; SO_4^{2-}, 31·4. $C_8H_{16}O_6N_2S_2$ requires C, 32·0; H, 5·3; N, 9·3; S, 21·4; SO_4^{2-}, 32·0%).

Methionine-methylsulphonium chloride. Methionine-methylsulphonium (methyl sulphate) (14·5 g.) was heated on a steam-bath for 3 hours with concentrated hydrochloric acid (130 c.c.). The sulphate was precipitated with barium chloride and filtered off. The filtrate was concentrated to dryness *in vacuo*, dissolved in water, and neutralised with pyridine. The solution was evaporated to dryness and triturated with hot ethanol to give the *chloride* (5·1 g., 48·3%), m. p. 134° (decomp.) (Found: C, 36·1; H, 7·0; N, 6·8; S, 15·5; Cl^-, 17·5%. $C_6H_{14}O_2SNCl$ requires C, 36·0; H, 7·0; N, 7·0; S, 16·0; Cl^-, 17·7%).

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