NOTES.

552. *The Action of Light on Diazoaminobenzene dissolved in Ethanol.*

By H. C. Freeman and R. J. W. Le Fèvre.

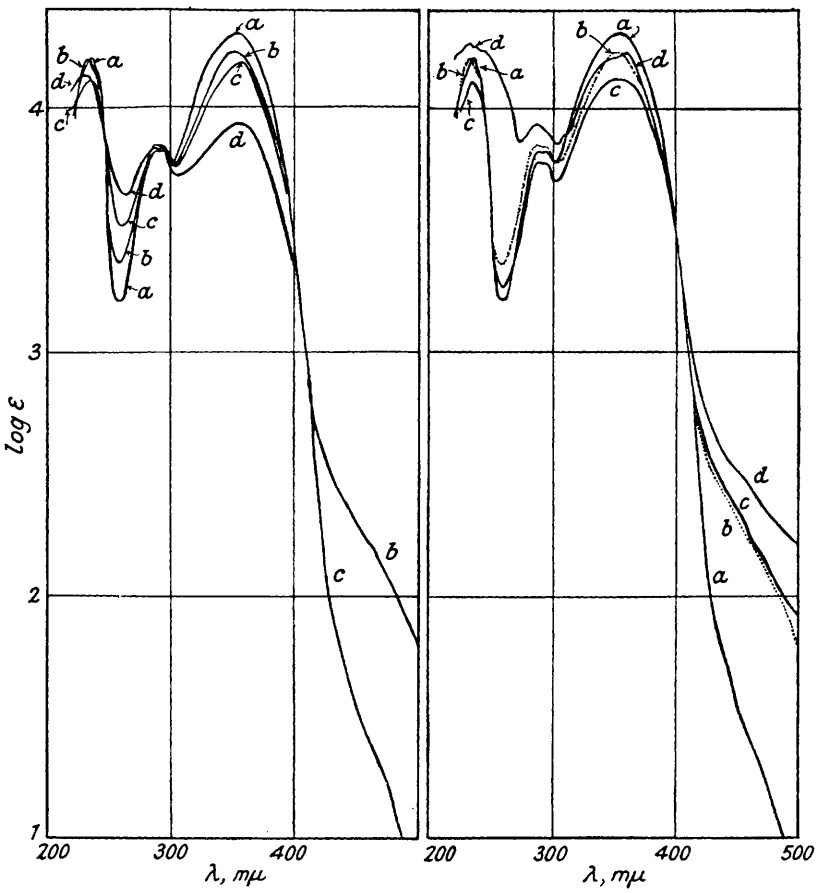
During investigations on geometrical isomerism among –N=N– compounds it has become apparent that, after illumination in solution, azobenzene (Winkel and Siebert, *Ber.*, 1941, **74**, 675; Hausser, *Z. Naturforsch.*, 1950, **5***a*, 56), aryl diazocyanides (Le Fèvre and Wilson, *J.*, 1949, 1106), aryl diazosulphonates (Freeman and Le Fèvre, *J.*, 1951, 415), and aryl diazocarboxyamides (Freeman and Le Fèvre, *J.*, 1951, 1977) all show alterations in the absorption spectrum which become partly reversed when the solutions are kept in darkness. In the last-mentioned case, the occurrence of reversible changes during illumination has been accepted as an indication of the probable presence of a labile isomer not yet isolated in the solid state. Although Le Fèvre and Vine (*J.*, 1937, 1805) showed that the dielectric constants of solutions of diazoaminobenzene in benzene were not seriously affected by illumination, experience (*e.g.*, Le Fèvre and Liddicoet, *J.*, 1951, 2743) has shown that on such evidence alone one cannot infer that the solute has persisted in its original condition. Accordingly the spectroscopic behaviour of alcoholic solutions of diazoaminobenzene has now been examined before and after illumination for varying periods, and again after storage in darkness.

The progressive modifications of the absorption spectrum are shown (Fig. 1) after exposures of 0, 35, 45, and 120 minutes (curves *a*, *b*, *c*, *d*) to the unfiltered radiation of a mercury-vapour lamp. From the spectra of the same solutions after storage in darkness

it was seen that the changes displayed in Fig. 1 were not due to a photochemically reversible process. For example, in Fig. 2 the absorption of the original solution (curve *a*) is compared with that recorded after 35 minutes' irradiation (curve *b*), followed in turn by those after 24 (curve *c*) and 120 hours' (curve *d*) storage in the dark.

The absorption initially observed for diazoaminobenzene corresponds to that reported previously (Wohl, *Bull. Soc. chim.*, 1938, **5**, 460), and is in general agreement with the known spectroscopic features of aryltriazens (Wohl, *loc. cit.*; Le Fèvre and Liddicoet, *loc. cit.*). Maxima occur at 236 ($\log_{10} \varepsilon = 4{\cdot}21$), 288 (3·82), 294 (3·82), and 355 mμ (4·30).

FIG. 1. FIG. 2.



Irradiation lowered the value of the extinction at 355 mμ, although increased absorption became evident at 260 and above 400 mμ. This trend continued after irradiation ceased (Fig. 2, *b* and *c*), emphasising the irreversibility of the transformation. Moreover, on prolonged storage, there were further marked alterations in the absorption, new bands appearing at 310 and 360 mμ, with general changes at other wave-lengths. The unknown *cis*-modification of diazoaminobenzene may be expected to have a polarity of the order of that of benzotriazole (*viz.*, 4·1 D; Jensen and Friediger, *Kgl. Danske Vidensk. Selsk.*, 1943, **20**, No. 20) so that any notable inversion of the ordinary form ($\mu = 0{\cdot}9$ D) should have been revealed by the experiments of Le Fèvre and Vine (*loc. cit.*). Since this was not so, it is concluded that diazoaminobenzene, by the present treatment, undergoes decomposition.

Finally we note that a *trans* ⟶ *cis*-change seems difficult from elementary steric considerations. A scale drawing shows interference between the amino-nitrogen and the

benzene ring of the theoretical *cis*-form, though this appears less serious than in similar drawings for the unstable isomers of the diazosulphonates (Freeman and Le Fèvre, *loc. cit.*). It may be mentioned that, except for the groups linked to the amine-nitrogen, this drawing and comment apply equally to the aryldimethyltriazens.

Experimental.—The solute was recrystallised from alcohol and had m. p. 98°. It was examined as 10^{-4}M-alcoholic solutions (10^{-5}M for the region near 350 mμ, 10^{-3}M above 400 mμ) with a Beckman photoelectric spectrophotometer, model DU. Irradiations were performed on 10^{-4}M-solutions in stoppered silica test-tubes held 30 cm. away from a 300-w, 240-v, "Hanovia" mercury-vapour lamp.

In preparing our scale diagrams we ignored the estimate of 141° (Le Fèvre and Vine, *loc. cit.*) for the angle between the two carbon–nitrogen bonds since this was based on a vector-additivity of bond-moments now known to be uncertain; instead, we used the following dimensions: Bond lengths (in Å): C_{ar}–C_{ar}, 1·40; C–H, 1·14; C–N, 1·45; N–H, 1·10; N–N, 1·48; N=N, 1·25. Bond-angles: Ar–N=N, 125°; Ar–N–N= or Ar–N–H, 110°. "Wirkungsradien" (in Å): N, 1·5; H, 1·2.

UNIVERSITY OF SYDNEY, N.S.W., AUSTRALIA. [*Received, January 3rd*, 1952.]

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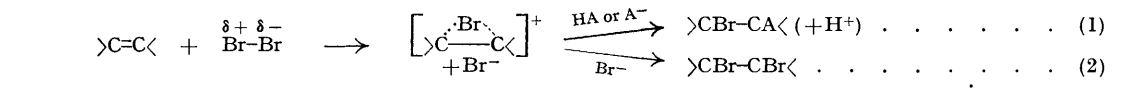
553. *Addition and Substitution with the Bromine Cation in Aqueous Solution.*

By D. C. ABBOTT and C. L. ARCUS.

REACTION between bromine and an olefin in the presence of a nucleophilic reagent HA or A^-, leading to the formation of the compound >CBr–CA<, proceeds as in (1):

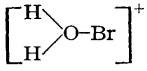


The bromine anion competes with the added nucleophilic reagent and in so far as the competition is successful the dibromide is formed (2).

It has been found (Derbyshire and Waters, *J.*, 1950, 573) that, when a silver salt is added to a solution of bromine in water or acetic acid containing sulphuric acid, bromine anion is removed as insoluble silver bromide and the reactions

$$Br_2 + H_2O \longrightarrow H^+ + Br^- + HOBr;\ HOBr + H^+ \longrightarrow H_2O + Br^+$$

are allowed to proceed, yielding a substantial concentration of bromine cations. The bromine cation is probably hydrated, and the hydrate (as annexed) is identical with hypobromous acid plus a proton.



This method (in addition to providing bromine cations) should, by the removal of bromine anions, increase the probability of reaction of an added nucleophilic reagent with the intermediate complex cation. The results recorded below for the interaction of bromine with styrene in aqueous acetic acid–sulphuric acid show that formation of 2-bromo-1-phenylethyl acetate is increased, and that of styrene dibromide decreased, by the presence of silver ion.

Attack of the bromine cation (prepared by the interaction of bromine, aqueous sulphuric acid, and silver nitrate) on α-phenylpropionic acid gave α-*p*-bromophenylpropionic acid; the bromine atom of this was not readily hydrolysed and oxidation yielded *p*-bromobenzoic acid. Some of the *o*-isomer may also have been formed; no substitution appeared to have occurred in the aliphatic part of the original acid.

Experimental.—Additions. (*a*) To a briskly-stirred suspension of silver acetate (17·0 g.) and styrene (10·4 g.; freshly distilled; b. p. 144—145°) in 6N-sulphuric acid (150 ml.) containing glacial acetic acid (50 ml.) a solution of bromine (16·0 g.) in glacial acetic acid (75 ml.) was added during 1½ hours. After a further ½ hour's stirring, the precipitated silver bromide (18·7 g., 100%) was separated by filtration through sintered glass, and the filtrate extracted with ether. The extract was washed with aqueous sodium carbonate and dried ($MgSO_4$) and the ether

removed. The product (13·1 g.) yielded fractions : (i) b. p. 84—86°/0·7 mm., n_D^{25} 1·5689 (2·7 g.); (ii) b. p. 91—95°/0·7 mm., n_D^{25} 1·5595 (5·4 g.) (Found : C, 48·3; H, 4·5; Br, 37·6. Calc. for a 83 : 17 mixture of $C_{10}H_{11}O_2Br$ and $C_8H_8Br_2$: C, 47·2; H, 4·3; Br, 37·5%); and (iii), b. p. 96—104°/0·7 mm., n_D^{25} 1·5560 (2·0 g.).

Fraction (ii) (1·8 g.) was heated under reflux with 3N-sodium hydroxide (10 ml.) for 6 hours. The solution was saturated with potassium carbonate and extracted with ether. The extract was dried (Na_2SO_4) and ligroin (b. p. 100—120°) added; needles, m. p. 62—64°, of phenylethylene glycol separated (0·9 g., 90%), which after recrystallisation from ether–ligroin had m. p. 64—65° alone and mixed with an authentic specimen of m. p. 64·5—65·5°. Similar hydrolysis of styrene dibromide (12·3 g.) with N-sodium hydroxide (135 ml.) for 6 hours yielded the glycol (1·3 g., 20%), m. p. 64—65°.

(*b*) From an experiment similar to (*a*), but without silver acetate, there was obtained a product (19·0 g.) which deposited styrene dibromide (6·0 g.), m. p. 68—70° (after recrystallisation from aqueous alcohol, m. p. 72—73° alone or mixed with an authentic specimen of m. p. 72—73°). The liquid product gave fractions : (i) b. p. 91—95°/1 mm. (5·9 g.), which on cooling deposited styrene dibromide (2 g.), m. p. 72—73°, and (ii) b. p. 96—97°/1 mm., n_D^{25} 1·5664 (3·3 g.).

(*c*) From an experiment similar to (*a*), but without silver acetate and with sodium bromide (20·6 g., 2 mols.) dissolved in the aqueous sulphuric acid, there was obtained styrene dibromide (11·9 g.), m. p. 68—71° (m. p. 72—73° after recrystallisation).

(*d*) To a mixture of styrene, acetic acid, and aqueous sulphuric acid, as in (*a*), bromine (16·0 g.) and glacial acetic acid (75 ml.) were added separately and simultaneously, with vigorous stirring. There was obtained styrene dibromide (16·1 g.), m. p. 71—73° (m. p. 72—73° after recrystallisation).

The yields of styrene dibromide isolated from (*a*), (*b*), (*c*), and (*d*) were respectively nil, 30, 45, and 61%.

Substitution. A solution of silver nitrate (8·5 g.) in water (50 ml.) was added dropwise during 1 hour to a well-stirred mixture of α-phenylpropionic acid (7·5 g.), bromine (8·0 g.), and 3N-sulphuric acid (150 ml.). Stirring was continued for 1 hour, the silver bromide was filtered off, and the filtrate and silver bromide were extracted with ether. The extract was dried (Na_2SO_4), the ether distilled off, and the viscous oil so obtained dissolved in aqueous sodium carbonate. This solution was extracted with ether then acidified, and again extracted. The latter extract was dried ($MgSO_4$) and the ether evaporated; the product on distillation yielded α-bromophenylpropionic acid (principally the *p*-isomer), b. p. 138—141°/1 mm., n_D^{25} 1·5594 (4·8 g.) (Found : C, 47·7; H, 4·1; equiv., 227·2. Calc. for $C_9H_9O_2Br$: C, 47·2; H, 4·0%; equiv., 229·0). The acid gave no bromide ion when heated for 15 minutes with alcoholic N-potassium hydroxide. The acid (2·95 g.) was heated under reflux for 1½ hours with potassium permanganate (10·0 g.) and sodium carbonate (5·0 g.) in water (150 ml.); concentrated hydrochloric acid (25 ml.) was added and sulphur dioxide passed in. The acid which separated was extracted with ether. The extract was dried (Na_2SO_4) and evaporated; the product (2·1 g., 80%) was thrice recrystallised from aqueous alcohol and yielded *p*-bromobenzoic acid, leaflets, m. p. 250—252° alone or mixed with an authentic specimen of m. p. 251—253°.

Thanks are expressed to the Department of Scientific and Industrial Research for a maintenance grant (to D. C. A.) and to Imperial Chemical Industries Limited for a grant.

BATTERSEA POLYTECHNIC, LONDON, S.W.11. [*Received, January 15th*, 1952.]

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554. *Purification of Yttrium by Precipitation with Sodium Nitrite.*

By O. M. HILAL and (in part) M. EL-ABBADY.

THE method of separation of yttrium recommended by Holden and James (*J. Amer. Chem. Soc.*, 1914, **36**, 638, 1418) and modified by Hopkins and Balke (*ibid.*, 1916, **38**, 2332) was based on hydrolysis of nitrite. Yttrium comes between neodymium and samarium in the order of basicity as determined by hydrolysis of their salts in presence of nitrite (Hopkins, *ibid.*, 1933, **55**, 3117, 3121) or by precipitation of their hydroxides by ammonium or sodium hydroxide.

The present authors found that the pH at initiation of nitrite precipitation increases with decreasing concentration of pure yttrium nitrate solution. For 0·7M- (80 g. of oxide/l.) and 0·35M-solutions the respective pH values were 6·2 and 6·4, of which the latter corresponds to pH 6·6 deduced from the curves of hydroxide precipitation of the rare-earth nitrate solutions by very dilute gaseous ammonia (Trombe, *Compt. rend.*, 1934, **216**, 888). Addition of sodium nitrite to a solution attaining a pH 6·2 does not alter its pH value and so precipitation depends wholly on hydrolysis.

Experimental.—The material used was crude yttria, containing a little erbia, kindly supplied by the late Professor S. Sugden (London University). The apparatus used for precipitation consisted of a round-bottomed flask connected to a steam generator. The volume of the solution was kept constant by distillation.

Preliminary experiment on the extent of precipitation with sodium nitrite showed that the range of pH 3—4 was favourable and to ensure complete precipitation addition of sodium nitrite was followed by passage of steam through the solution for 2 hours after the first appearance of turbidity. The precipitate obtained was crystalline.

The analysis of the precipitate obtained on treating chemically pure yttrium nitrate solution with sodium nitrite, as cited below, gave Y_2O_3 61·2, N_2O_5 17·38, and H_2O 21·42% (by difference). This composition may be represented by the formula $3Y_2O_3,2N_2O_5,15H_2O$. Traces of nitrous anhydride were present and were included as nitric anhydride (Fogg and James, *J. Amer. Chem. Soc.*, 1922, **44**, 311).

General procedure. The oxide was dissolved in nitric acid, evaporated to dryness, and diluted to 80 g./l. The pH of the solution was adjusted between 3 and 4 by adding a few drops of dilute aqueous ammonia. To the boiling solution was then added a weight of solid sodium nitrite double that of the oxide expected to be present in the precipitated fraction, and steam was passed through the solution as specified above. When fractionation was carried out in series, the head-fraction precipitate of the first series was dissolved in nitric acid, evaporated to dryness, then adjusted to 80 g. oxide/l., and similarly treated; this afforded the head fraction of the second series. When the required fraction had been precipitated and filtered off, the second fraction of the first series, after being dissolved in nitric acid and evaporated to dryness, was added to the filtrate; the pH of the mixed solution was not less than 3.

The equivalent was determined by the method used by Hilal and Sugden (*J.*, 1949, 135).

300 G. of oxide (equiv., 38·29) were fractionated (39 times in 7 series) and the tail fraction (62 g.; equiv., 37·82) was fractionated 27 times in 4 series. The last series was split into 10 fractions. The tail fraction (10·8 g. of oxide of equiv. 37·64) was found to be spectroscopically equivalent to the pure yttria of $10^6\chi_{Y^{3+}} = 0·21$ previously prepared by Hilal and Sugden (*loc. cit.*). It did not show the persistent lines of holmium and erbium.

The efficiencies of separation by (*a*) the ferricyanide (March, *J.*, 1947, 118) and (*b*) the nitrite methods have been compared. Part of an oxide (equiv., 38·64; 80 g./l.) was fractionally precipitated 23 times (four series on 4, 5, 6, and 8 fractions) by each method. The Table shows results for the last series. The final fraction (8) was the unprecipitated portion remaining in the mother-liquor and was recovered as hydroxide.

Fraction no. (head = 1)	(*a*)		(*b*)	
	Equiv.	% (wt.)	Equiv.	% (wt.)
1	40·30	15	40·24	9
2	39·28	14	39·20	10
3	38·84	13	39·01	22 *
4	38·66	14	38·68	12
5	38·60	13	38·59	14
6	38·58	14	38·42	16
7	38·40	12	38·33	10
8	38·31	5	38·22	7

* The volume was reduced.

The spectroscopic work was carried by Mr. Z. Saweris (Government Laboratory, Cairo) to whom the authors tender thanks.

FAROUK I UNIVERSITY, MOHARRAM BAY, ALEXANDRIA. [*Received, February 9th*, 1952.]

555. *The Triterpenoids of* Alstonia verticillosa.

By O. C. MUSGRAVE and H. M. WAGNER.

DURING an investigation of the alkaloids of *Alstonia verticillosa*, Sharp (*J.*, 1934, 1227) obtained a crystalline " sterol " fraction from the alcohol-soluble portion of the petroleum extract of the bark; the presence of lupeol in this fraction was suspected. We have now examined this material which was made available to us through the courtesy of Dr. T. A. Henry. The crystalline solid described by Sharp was hydrolysed and benzoylated. Chromatography of the products on alumina readily gave lupenyl benzoate and a mixture of α- and β-amyrenyl benzoates which was in turn separated by crystallisation. The identities of these compounds were confirmed by conversion into the corresponding acetates. The occurrence of lupeol in the latex of *A. scholaris* and of α- and β-amyrin in Malabuwai gutta percha from *A. grandifolia* has previously been reported (Ultée, *Chem. Weekbl.*, 1914, **11**, 456; Hillen, *Arch. Pharm.*, 1913, **251**, 94).

Experimental.—Chromatography of the mixed benzoates. A solution of the crystalline solid (m. p. 180—190°; 2·75 g.) from *A. verticillosa* in benzene (12 ml.) was heated under reflux on the steam-bath for 20 hours with methanolic potassium hydroxide (5%; 100 ml.). After being worked up in the usual manner, the product was benzoylated on the steam-bath with pyridine (7 ml.) and benzoyl chloride (3·5 ml.). A solution of the resulting mixed benzoates (3 g.) in light petroleum (60—80°; 100 ml.) was filtered through a column of alumina (Grade II, Brockmann; 3 × 23 cm.) which was washed with light petroleum–benzene (20 : 1). The first fraction (2400 ml. of eluate; 1·64 g.; m. p. 186—198°) was readily separated into two parts by fractional crystallisation from benzene–ethanol. The less soluble of these, β-amyrenyl benzoate (0·69 g.) was obtained as plates (Found: C, 83·7; H, 10·4. Calc. for $C_{37}H_{54}O_2$: C, 83·7; H, 10·3%). The more soluble material, α-amyrenyl benzoate (0·2 g.), separated in prisms (Found: C, 83·8; H, 10·6%). The more strongly adsorbed fraction (1300 ml. of eluate; 0·59 g.; m. p. 222—231°) crystallised from benzene–ethanol, giving lupenyl benzoate (0·3 g.) as plates (Found: C, 83·7; H, 10·7%).

α-Amyrenyl, β-amyrenyl, and lupenyl acetates. The benzoates were separately hydrolysed on the steam-bath in benzene solution with methanolic potassium hydroxide (5%). The alcohols obtained were acetylated by acetic anhydride and pyridine on the steam-bath. In this way, β-amyrenyl acetate was obtained as needles from ethanol (Found: C, 82·0; H, 11·0. Calc. for $C_{32}H_{52}O_2$: C, 82·0; H, 11·1%), and α-amyrenyl acetate (Found: C, 82·1; H, 11·0%) and lupenyl acetate as needles from methanol–chloroform (Found: C, 81·9; H, 11·1%).

	This work		Previously recorded	
	M. p.	$[\alpha]_D^{18}$ in $CHCl_3$	M. p.	$[\alpha]_D^{18}$ in $CHCl_3$
β-Amyrenyl benzoate	232°	+98° (c = 1·3)	234—235° (1)	+100° (2)
β-Amyrenyl acetate	240	+82·5 (c = 0·5)	240—241 (1)	+81·4 (1)
α-Amyrenyl benzoate	198	+94 (c = 1·3)	194 (1)	+94·6 (2)
α-Amyrenyl acetate	225	+75 (c = 0·8)	224—225 (1)	+76 (1)
Lupenyl benzoate	262	+63 (c = 0·8)	261·5 (3)	+61·2 (1)
Lupenyl acetate	214	+47 (c = 0·9)	214 (3)	+47·5 (3)

(1) Cohen, *Rec. Trav. chim.*, 1909, **28**, 368, 391. (2) Zinke, Friedrich, and Rollet, *Monatsh.*, 1920, **41**, 253. (3) Heilbron, Moffett, and Spring, *J.*, 1934, 1583.

The authors thank Professor F. S. Spring, F.R.S., for his interest during this work, and the Department of Scientific and Industrial Research for a maintenance grant (to H. M. W.).

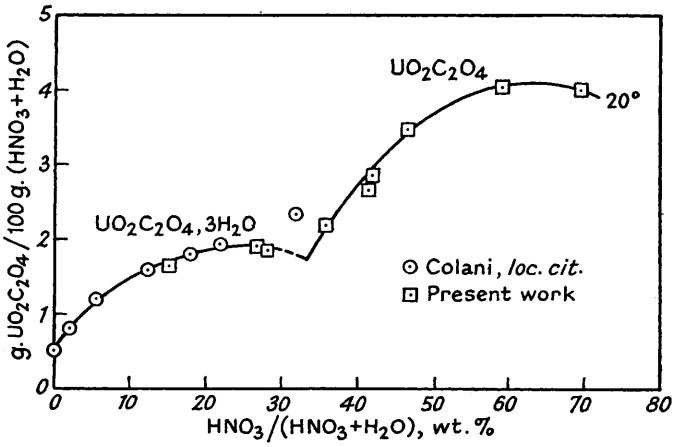
THE ROYAL TECHNICAL COLLEGE, GLASGOW. [*Received, March 6th*, 1952.]

556. *The Solubility of Uranyl Oxalate in Nitric Acid.*

By C. B. Amphlett and (Mrs.) O. T. Davidge.

The solubility of uranyl oxalate in nitric acid has been measured by Colani (*Bull. Soc. chim.*, 1925, **37**, 859) at acidities up to 31% by weight. We have extended these measurements to 70% nitric acid in order to find if the salt undergoes dehydration similar to that observed in the case of uranyl nitrate in concentrated nitric acid (*idem, ibid.*, 1926, **39**, 1243).

Uranyl oxalate trihydrate was prepared by precipitation from aqueous uranyl nitrate solutions with sodium oxalate; the precipitate was filtered off, washed free from nitrate, and dried at 60°. Analysis for uranium and for oxalate corresponded to the trihydrate, which is the form normally precipitated from aqueous solutions (Gmelin's " Handbuch," 8th edn., S.N. 55, p. 168).



Solubilities at room temperature were determined by shaking an excess of the solid with nitric acid of the required concentration for several days, in long-necked flasks with securely waxed stoppers; preliminary experiments showed that two days sufficed to ensure saturation, and that the rate of decomposition of oxalic acid by nitric acid was too low to cause any displacement of equilibria set up in solution. The temperature of these measurements was 20° ± 1°. After being shaken, the solution was allowed to settle; aliquots were taken, diluted, and analysed for uranium and for free acid content (after removal of uranium as peroxide, no correction being made for the hydrogen-ion content thereby introduced, this being small compared with the acidity due to nitric acid). The density of the final solution was measured by direct weighing of a known volume.

The results, expressed as g. of anhydrous $UO_2C_2O_4$ per 100 g. of (HNO_3 + H_2O) are given below as a function of the acid concentration (g. per 100 g. of solvent) :

HNO_3/(HNO_3 + H_2O), wt. %	15·1	26·8	27·9	35·8	41·5	42·0	46·5	58·9	69·5
$UO_2C_2O_4$, g./100 g. (HNO_3 + H_2O) ...	1·63	1·88	1·87	2·19	2·68	2·84	3·48	4·04	3·99

These results, together with those of Colani (*loc. cit.*), are plotted on the accompanying figure; apart from one value at 31 wt. % HNO_3 the agreement is good. The solubility curve shows two branches, due to dehydration of the trihydrate at higher acid concentrations. Attempts to determine the composition of the solid phase by direct analysis were only partly successful, owing to difficulties encountered in removing adsorbed liquid from the solid without washing. One good duplicate determination was obtained at 59% HNO_3, indicating that the solid phase was anhydrous $UO_2C_2O_4$. We would expect the lower branch of the curve to correspond to the trihydrate, by analogy with the case of solutions containing no free acid; this was confirmed by comparison of the initial and final acidities of the solution. If a known excess of trihydrate is used the initial acidity will be diluted by 3 moles of water per mole of trihydrate dissolved, plus n moles of water per mole remaining undissolved, where the final solid phase has the composition

$UO_2C_2O_4,(3 - n)H_2O$. Comparisons of this type suggested that $n \simeq 0$ over the first branch of the curve, and $n \simeq 3$ over the second branch. It seems reasonable to assume that the two branches correspond to $UO_2C_2O_4,3H_2O$ and $UO_2C_2O_4$ respectively (cf. uranyl nitrate).

We thank Sir John Cockcroft, F.R.S., for permission to publish this information.

CHEMISTRY DIVISION, ATOMIC ENERGY RESEARCH ESTABLISHMENT,
HARWELL, BERKS. [*Received, March 6th*, 1952.]

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557. *The Structure of the Aminopyridines.*

By J. D. S. GOULDEN.

ANGYAL and ANGYAL (*J.*, 1952, 1461) have shown that α- and γ-amino-*N*-heterocyclic compounds exist in the amino- and not in the tautomeric imino-form. Their conclusions were drawn from the chemical reactions and pK_a values of the compounds. The infra-red absorption spectra of the aminopyridines in the 3-μ region confirm these views, and show that in 2- and 4-aminopyridines the resonance forms containing the $=\overset{+}{N}H_2$ configuration make considerable contributions to the molecular structure.

The Table shows the values obtained for the NH frequencies of the three aminopyridines, together with those of the two isomeric methyl derivatives of 2-aminopyridine. The NH frequencies of aniline, 2-aminopyrimidine, and *p*-nitroaniline were also examined and their values are listed. The absorption spectra of the solids in this region of the spectrum were found to be quite different from those in solution, owing to hydrogen bonding and other intermolecular effects.

NH *frequencies* (*cm.*$^{-1}$) *of some bases in carbon tetrachloride* (*cell length*, 5 cm.). (ε_{molar} *in parentheses*, ±10%).

Compound	—NH_2 frequencies		>NH frequency	=NH frequency
Aniline	3480 (133)	3396 (179)	—	—
2-Aminopyridine	3509 (51)	3411 (79)	—	—
3- ,,	3482 (38)	3396 (56)	—	—
4- ,,	3508 (47)	3413 (86)	—	—
2-Methylaminopyridine	—	—	3450 (100)	—
1 : 2-Dihydro-2-imino-1-methylpyridine	—	—	—	3323 (30)
2-Aminopyrimidine	3541 (71)	3431 (117)	—	—
p-Nitroaniline	3508 (52)	3417 (148)	—	—

The appearance of a pair of frequencies at about 3400 and 3500 cm.$^{-1}$ confirms the amino-structure of 2- and 4-aminopyridine. If these compounds existed in the imino-forms, frequencies at about 3400 and 3300 cm.$^{-1}$ would have been expected as in 1 : 2-dihydro-2-imino-1-methylpyridine and 2-methylaminopyridine.

Flett (*Trans. Faraday Soc.*, 1948, **44**, 767) showed that introduction of electron-attracting groups into the benzene nucleus of aniline increased the values of both NH_2-frequencies, and that that of electron-repelling groups decreased them. Similarly, in the aminopyridines, attraction of electrons by the ring-nitrogen atom increases the contribution of the $=\overset{+}{N}H_2$ type structure with respect to —NH_2, as shown by the NH_2 frequency value in the series :

Aniline, 3-aminopyridine ⟶ 2- and 4-Aminopyridine ⟶ 2-Aminopyrimidine

Except for aniline, this series shows a rise in ε_{molar} values for the NH_2 absorption frequencies, parallel to the rise in frequency values.

The NH_2 frequency values of 3-aminopyridine are close to those of aniline, so that it is to be expected that the chemical reactions of the amino-group in 3-aminopyridine will resemble those of aniline. Flett (*loc. cit.*) reported the values of the NH_2 frequencies for

p-nitroaniline to be 3535 and 3436 cm.$^{-1}$, but re-examination of this compound with the grating spectrometer used here gave values of 3508 and 3417 cm.$^{-1}$. Thus the electron-attracting power of the nitro-group in *p*-nitroaniline is similar to that of the ring-nitrogen atom in 2- and 4-aminopyridine.

Gordy (*J. Amer. Chem. Soc.*, 1940, **62**, 497) showed, by infra-red spectroscopy, that ethers are able to form hydrogen bonds with amines. Since the ultra-violet measurements by Anderson and Seeger (*ibid.*, 1949, **71**, 340) were made on dioxan solutions, the ultra-violet absorption spectra of 2- and 3-aminopyridine in carbon tetrachloride were examined as part of this investigation. Although the absorption of the solvent vitiated measurements at wave-lengths below 250 mμ, maxima were found at 292 (log ε_{molar} 3·54) and 294 mμ (log ε_{molar} 3·52) for 2- and 3-aminopyridine respectively. Since Anderson and Seeger reported that both compounds had maxima at about 298 mμ (log ε_{molar} ~3·65), it can be seen that this hydrogen bonding has little effect on the position and intensity of the ultra-violet absorption maxima.

Experimental.—The infra-red absorption spectra were examined with a Grubb Parsons S.3 spectrometer, with a 2904 lines/inch replica diffraction grating (Goulden, *J. Sci. Instr.*, in the press). Calibration points in the 3-μ region were obtained from the gaseous ammonia spectrum (Dennison and Hardy, *Phys. Review*, 1932, **39**, 938) and the frequencies listed in the Table are considered to be accurate to ±2 cm.$^{-1}$. The ultra-violet spectra were examined with a Unicam S.P. 500 spectrometer, with 1-cm. and 1-mm. quartz absorption cells. The compounds used in this investigation were purified by distillation and crystallisation until their m. p.s were in accord with those recorded in the literature.

The author thanks Mr. B. Peutrell for examining the ultra-violet absorption spectra and for recrystallising some of the compounds.

Biochemistry Research Dept., Boots Pure Drug Co., Ltd.,
Island Street, Nottingham. [*Received, March 12th*, 1952.]

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558. *Some Derivatives of 2 : 6-Dihydroxybenzoic Acid.*

By R. D. Watson.

The therapeutic action of sodium 2 : 6-dihydroxybenzoate (sodium γ-resorcylate) in rheumatic fever has been investigated in an attempt to explain the activity of certain hydroxybenzoic acids, notably salicylic acid, in this disease. In a preliminary account of this work sodium 2 : 6-dihydroxybenzoate has been stated to be more active than sodium salicylate (Reid, Watson, Cochran, and Sproull, *Brit. Med. J.*, 1951, II, 321). Reference to the chemical availability of sodium 2 : 6-dihydroxybenzoate and some of its derivatives may thus be timely.

The most convenient methods of preparation of 2 : 6-dihydroxybenzoic acid at present in the literature are those of Mauthner (*J. pr. Chem.*, 1929, **121**, 261; 1930, **124**, 319) and Limaye (*J. Indian Chem. Soc.*, 1935, **12**, 788). The latter method was first used, but was later rejected on account of the need for fractional crystallisation to purify the 8-acetoxy-7-hydroxy-4-methylcoumarin. Mauthner's method gave an overall yield of 5% from *m*-dinitrobenzene, but this is increased to 11% if in the final stage the demethylation product in iced water is merely filtered off, the benzene separated, and the aqueous layer acidified with concentrated hydrochloric acid to precipitate the 2 : 6-dihydroxybenzoic acid.

The sodium salt of the acid is readily obtained by heating a solution of the acid (10 g.) in N-sodium hydrogen carbonate (30 c.c.) at 60—70° and slowly adding solid sodium hydrogen carbonate (2·5 g.). The sodium salt is precipitated on cooling and is recrystallised from 0·5N-sodium hydrogen carbonate solution.

Ethyl and n-*propyl* 2 : 6-*dihydroxybenzoate* were prepared by saturating a solution of the acid (5 g.) in the appropriate alcohol (100 c.c.) with dry hydrogen chloride, and refluxing the whole for 8 hours. They were purified by recrystallisation from dilute methyl alcohol (see table).

	M. p.	Found C, %	Found H, %	Formula	Required C, %	Required H, %
Esters of 2 : 6-*dihydroxybenzoic acid*						
Ethyl	50—51°	59·2	5·5	$C_9H_{10}O_4$	59·3	5·5
n-Propyl	38—39	61·0	6·5	$C_{10}H_{12}O_4$	61·2	6·2
Esters of 2 : 6-*dimethoxybenzoic acid*						
Ethyl	71—72	62·8	6·7	$C_{11}H_{14}O_4$	62·8	6·7
n-Propyl	37—38	64·4	7·1	$C_{12}H_{16}O_4$	64·2	7·2
n-Amyl	47—48	66·4	7·8	$C_{14}H_{20}O_4$	66·6	8·0
n-Hexyl	48—49	67·4	8·2	$C_{15}H_{22}O_4$	67·6	8·3

The *esters* of 2 : 6-dimethoxybenzoic acid listed in the table were prepared by refluxing the acid (5 g.) with the appropriate alcohol (20 g.) and concentrated sulphuric acid (0·25 c.c.) and were recrystallised from dilute methyl alcohol.

Through the good offices of the Medical Research Council, arrangements were made for the preparation in the Chemical Research Laboratory of the Department of Scientific and Industrial Research of the larger amounts of sodium γ-resorcylate required for more extensive clinical trial.

I thank Professor J. W. Cook, F.R.S., and Professor Sir John McNee for their advice and interest in this work, and Mr. J. M. L. Cameron for the microanalyses.

MEDICAL RESEARCH COUNCIL, CLINICAL CHEMOTHERAPEUTIC RESEARCH UNIT,
GARDINER INSTITUTE OF MEDICINE,
THE UNIVERSITY, GLASGOW, W.2. [*Received, March 19th,* 1952.]

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559. *The Formation of* 3-*Methyl* 1 : 2-iso*Propylidene Xylofuranose.*

By R. A. LAIDLAW.

THE di*iso*propylidene derivatives of the hexoses and pentoses may be divided into two classes: (*a*) the pyranoses, such as 1 : 2-3 : 4-di*iso*propylidene galactopyranose and 1 : 2-4 : 5- and 2 : 3-4 : 5-di*iso*propylidene fructopyranoses and (*b*) the furanoses, *e.g.*, 2 : 3-5 : 6-di*iso*propylidene mannofuranose, 1 : 2-5 : 6-di*iso*propylidene glucofuranose, and 1 : 2-3 : 5-di*iso*propylidene xylofuranose.

The preparation of group (*b*) derivatives from the corresponding simple sugars involves a ring change from the pyranose to the furanose form, and the present investigations are an attempt to elucidate the course of this transformation. Two possibilities suggest themselves, (1) that ring-change takes place solely to facilitate entry of one particular *iso*propylidene substituent (at the 5 : 6-positions with mannose and glucose and at the 3 : 5-positions with xylose), this reaction being " independent " of reaction at the 1 : 2-positions, or (2) that the sugar, in contact with acetone under the given conditions, assumes the furanose form before reaction, condensation then taking place directly. This latter alternative implies increased reactivity in the furanose form, presumably due to the configuration of the molecule.

If (1) is correct it should be possible to prepare directly a more stable pyranose derivative of a group (*b*) sugar by " blocking " a reactive position with an inert substituent. In this manner 3-methyl D-xylopyranose would yield 3-methyl 1 : 2-*iso*propylidene D-xylopyranose.

To test this theory 3-methyl D-xylopyranose (Levene and Raymond, *J. Biol. Chem.*, 1933, **102**, 332) was treated with acetone. The product was a syrup having the properties of a methyl mono*iso*propylidene xylose, which on methylation with methyl iodide and silver oxide yielded a dimethyl mono*iso*propylidene xylose; $[\alpha]_D^{17}$ −60° (in chloroform) [a sample of authentic 3 : 5-dimethyl 1 : 2-*iso*propylidene D-xylose (Levene and Raymond, *loc. cit.*) showed $[\alpha]_D^{17}$ −56° (in chloroform)]. Hydrolysis with dilute acid gave a dimethyl D-xylose, which was purified by separation on a column of cellulose (Hough, Jones, and Wadman, *J.*, 1949, 2511). Apart from very small amounts of impurities, this product appeared to consist entirely of one component, with the same R_G value on a paper chromatogram as 3 : 5-dimethyl xylose.

Oxidation with bromine in water gave a lactone which was very slowly hydrolysed in water, indicating a γ-lactone. The changes in specific rotation during hydrolysis corre-

sponded closely to those found for authentic 3 : 5-dimethyl D-xylonolactone, and were entirely different from those previously recorded for 3 : 4-dimethyl D-xylonolactone (James and Smith, *J.*, 1945, 739). Furthermore, oxidation with sodium periodate (Reeves, *J. Amer. Chem. Soc.*, 1941, **63**, 1476) gave no formaldehyde, indicating that either or both hydroxyl groups on $C_{(4)}$ and $C_{(5)}$ were substituted.

It is therefore apparent that the product is 3 : 5-dimethyl D-xylofuranose, and that condensation of 3-methyl D-xylose with acetone has yielded 3-methyl 1 : 2-*iso*propylidene D-xylofuranose. There was no evidence of the simultaneous formation of the corresponding pyranose derivative. This result demonstrates that change of ring form is induced by the greater reactivity of xylose in the furanose form under these conditions, and that the transformation is not effected solely to allow condensation at the 3 : 5-positions.

Similar results should be obtained with glucose and mannose derivatives, while galactose and fructose should yield pyranose derivatives.

Experimental.—All evaporations were conducted under diminished pressure; all temperatures recorded are bath-temperatures. Fractions from the cellulose column were dissolved in water, and the solution filtered and evaporated to dryness; the product was redissolved in acetone and the solution evaporated to yield the purified fraction.

3-*Methyl* D-*xylose*. This was prepared *via* 1 : 2-*iso*propylidene 5-trityl D-xylose (Levene and Raymond, *loc. cit.*). 3-Methyl D-xylose was obtained as a syrup which was purified by chromatography on a column of cellulose. The crystalline product had m. p. and mixed m. p. 98—101° (Found : OMe, 17·5. Calc. for $C_6H_{12}O_5$: OMe, 18·9%).

3-*Methyl* 1 : 2-iso*propylidene* D-*xylofuranose*. 3-Methyl D-xylose (1·40 g.) was dissolved in AnalaR acetone (100 c.c.), concentrated sulphuric acid (0·5 c.c.) and anhydrous copper sulphate (10 g.) were added, and the mixture was shaken for 24 hours at room temperature. After the addition of water (1 c.c.) the solution was neutralised with calcium hydroxide and filtered. Evaporation then yielded a syrup which failed to crystallise. Distillation of this material at 135—140°/0·05 mm. over barium carbonate gave a clear colourless liquid (1·15 g.), n_D^{18} 1·4600, $[\alpha]_D^{18}$ −64° (*c*, 1·73 in chloroform) (Found : CMe_2, 18·4. $C_9H_{16}O_5$ requires CMe_2, 20·6%).

3 : 5-*Dimethyl* 1 : 2-iso*propylidene* D-*xylofuranose*. The monomethyl derivative (1·05 g.) was methylated four times with methyl iodide and silver oxide, and the final product was dissolved in acetone. After filtration, the solution was evaporated to dryness and the syrup dried (P_4O_{10}) at 35°/0·05 mm. for 1 hour. The product (0·90 g.) showed n_D^{15} 1·4461, $[\alpha]_D^{17}$ −60° (*c*, 1·09 in chloroform) (Found : OMe, 28·9. Calc. for $C_{10}H_{18}O_5$: OMe, 28·4%).

3 : 5-*Dimethyl* D-*xylofuranose*. Dimethyl *iso*propylidene D-xylose (0·80 g.) was heated with sulphuric acid (1% wt./vol.; 25 c.c.) at 100°. The material was not sufficiently soluble to enable a measurement of specific rotation to be taken at zero time; the solution showed $[\alpha]_D^{18}$ +19° after 30 minutes (constant value). Neutralisation of the solution with barium carbonate, filtration, and evaporation of the filtrate yielded a product which was exhaustively extracted with boiling acetone. Evaporation of the extract gave a syrup (0·55 g.). Examination on the paper chromatogram showed the fraction to be composed mainly of a dimethyl xylose with an R_G value slightly greater than that of 2 : 3-dimethyl xylose, together with small amounts of other components. The syrup (0·50 g.) was purified by chromatography on a column of cellulose (15″ × 1·3″) (Hough, Jones, and Wadman, *loc. cit.*), butanol–light petroleum (b. p. 100—120°) (1 : 1) saturated with water being used as solvent. This treatment gave fractions : (*a*) R_G value corresponding to trimethyl xylopyranose (trace); (*b*) R_G value *ca.* 0·85 (trace); (*c*) R_G value *ca.* 0·78 (0·44 g.; main fraction); (*d*) R_G value corresponding to 2 : 3-dimethyl xylose (trace); and (*e*) R_G value corresponding to 3-methyl xylose (*ca.* 0·04 g.). The recovery was 98—100%.

Fraction (*c*) had the same R_G value as authentic 3 : 5-dimethyl D-xylose (see below); it showed $[\alpha]_D^{17}$ + 11° (*c*, 0·84 in chloroform), +25° (*c*, 1·13 in water) (Found : OMe, 33·0. Calc. for $C_7H_{14}O_5$: OMe, 34·8%).

3 : 5-*Dimethyl* D-*xylonolactone*. The syrupy fraction (*c*) (0·10 g.) was oxidised with bromine in water for 4 days at room temperature, by which time the solution, after removal of bromine by aeration, was non-reducing to Fehling's solution. After neutralisation with silver carbonate the solution was filtered and treated with hydrogen sulphide to remove silver. Filtration, aeration, and evaporation yielded a syrup which was heated at 100°/18 mm. for ½ hour and then distilled at 140—150°/0·07 mm. over barium carbonate. The product (30 mg.) showed $[\alpha]_D^{17}$ +72° (zero time), +69° (1 hour), +65° (3 days), +62° (7 days), +58° (17 days), +51° (31 days), +41° (48 days) (*c*, 0·725 in water).

Periodate oxidation of the lactone from fraction (c). A small quantity of the lactone solution was treated with N/5-sodium hydroxide (0·5 c.c.) at 50° for 15 minutes. Periodate oxidation of the resulting sodium salt of the acid (Reeves, *loc. cit.*) yielded no formaldehyde, since there was no colour with acid phenylhydrazine–ferricyanide.

Preparation of a sample of authentic 3 : 5-*dimethyl* D-*xylonolactone*. 1 : 2-*iso*Propylidene D-xylose was methylated with the Purdie reagents, and the product was hydrolysed, yielding 3 : 5-dimethyl D-xylose (Levene and Raymond, *loc. cit.*) which was purified by chromatography on cellulose. Oxidation of this material under conditions similar to those described above and distlllation of the product gave 3 : 5-dimethyl D-xylonolactone; $[\alpha]_D^{17}$ +79° (zero time), +76° (6 hours), +62° (7 days), +54° (16 days) (*c*, 1·61 in water).

The author thanks Professor E. L. Hirst, F.R.S. for his interest in this work.

KING'S BUILDINGS, UNIVERSITY OF EDINBURGH. [*Received, March 28th*, 1952.]

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560. *Attempted Preparation of* 2 : 4-*Dinitrobenzenesulphinic Acid.*

By HELENA BRADBURY and F. J. SMITH

WE have failed to prepare 2 : 4-dinitrobenzenesulphinic acid from 2 : 4-dinitrobenzenesulphonylhydrazide by the method recorded by Davies, Storrie, and Tucker (*J.*, 1931, 624).

Sodium 2 : 4-dinitrobenzenesulphonate (E. Erdmann and H. Erdmann, D.R.-P., 65,240) was converted by phosphorus pentachloride at >100° (marked decomposition at higher temps.) into the sulphonyl chloride which, recrystallised from benzene–light petroleum, melted at 102° and for identification was converted into the amide, m. p. 154° (Willgerodt and Mohr, *J. pr. Chem.*, 1886, **34**, 123, record m. p. 102° and 154° respectively).

In the preparation of the sulphonylhydrazide we found it better to add alcoholic hydrazine hydrate to a benzene solution of the chloride (2·66 g.) at approx. −10°, thereby reducing the tendency towards the formation of 2 : 4-dinitrophenylhydrazine; after crystallisation from dioxan–water at 0°, the yield was 1·09 g. Violent decomposition occurred when the material was heated to 113°. Davies *et al.* (*loc. cit.*) give m. p. 110° (decomp.) and a lower yield. We isolated the 2 : 4-dinitrophenylhydrazine hydrochloride, m. p. 186° (decomp.), when the sulphonyl chloride in benzene was added to alcoholic hydrazine hydrate. Rise in temperature favours displacement of the chlorosulphonyl group from the aromatic nucleus by hydrazine in both methods of preparation, and from a warm alcoholic solution of the reactants 2 : 4-dinitrophenylhydrazine appeared to be the sole product.

On warming of the sulphonyl hydrazide with 2N-hydrochloric acid at *ca.* 80°, filtration from insoluble matter, and acidification with concentrated hydrochloric acid, only octahedral crystals of hydrazine dihydrochloride, m. p. 197°, were precipitated.

Drs. Storrie and Tucker have since written to us : " We agree that 2 : 4-dinitrobenzenesulphinic acid cannot be obtained by the method we described. We can no longer support Mr. Buchanan's claim to have isolated a sulphur-containing compound."

Dann and Davies (*J.*, 1929, 1051) prepared a number of sulphinic acids from the appropriate sulphonyl chloride and hydrazine hydrate at various temperatures, but not directly from the pure, isolated sulphonyl hydrazides. We think it is possible that the sulphinic acids may arise from interaction between sulphonyl chloride and sulphonylhydrazide thus :

$$R{\cdot}SO_2Cl + R{\cdot}SO_2{\cdot}NH{\cdot}NH_2 = 2R{\cdot}SO_2H + N_2 + HCl$$

since Dann and Davies proved that the gas evolved during the reaction contained no hydrogen. This could not be the case if simple decomposition of the sulphonylhydrazide took place :

$$R{\cdot}SO_2NH{\cdot}NH_2 = R{\cdot}SO_2H + N_2 + H_2$$

It may well be, however, that the reaction is more complicated than that shown in the former equation (*vide* Curtius and Lorenzen, *J. pr. Chem.*, 1898, **58**, 166).

COLLEGE OF TECHNOLOGY, LIVERPOOL. [*Received, April 4th*, 1952.]

561. *Formation of Flavanthrones from Derivatives of 2-Aminoanthraquinone.*

By WILLIAM BRADLEY and HARRY E. NURSTEN.

IT has been shown (*J.*, 1951, 2070) that 3 : 3′-di-*tert.*-butylflavanthrone is formed by the action of sodium acetate and copper acetate on 2-amino-1-bromo-3-*tert.*-butylanthraquinone. Continuing these experiments we have found that when the time of the reaction is reduced to two hours 3 : 3′-di-*tert.*-butylflavanthrone is no longer obtained. When, however, an equimolecular mixture of 2-amino-3-*tert.*-butylanthraquinone and its 1-bromo-derivative is heated under the same conditions the formation of 3 : 3′-di-*tert.*-butylflavanthrone again takes place. The result suggests that the formation of the flavanthrone by the action of copper acetate and sodium acetate on the bromo-derivative alone involves two reactions : debromination of a portion and condensation of the debrominated product with unchanged bromo-derivative. The second reaction is analogous to the β-methylation of indole by means of methyl iodide (Weissgerber, *Ber.*, 1910, **43**, 3521).

Experimental.—Self-condensation of 2-amino-1-bromo-3-tert.-butylanthraquinone. The experiments described in *J.*, 1951, 2176—2177 were repeated, the heating being carried out for only 2 hours. The following compounds were isolated by chromatography : 3 : 3′-di-*tert.*-butylindanthrone (0·048 g.), 3 : 3′-di-*tert.*-butylindanthroneazine (0·021 g.), and 2-amino-3-*tert.*-butylanthraquinone (0·013 g.); neither 2 : 2′-diamino-3 : 3′-di-*tert.*-butyl-1 : 1′-dianthraquinonyl nor 3 : 3′-di-*tert.*-butylflavanthrone was present in the product.

Condensation of 2-amino-1-bromo-3-tert.-butylanthraquinone with 2-amino-3-tert.-butylanthraquinone. 2-Amino-3-*tert.*-butylanthraquinone (0·05 g.), 2-amino-1-bromo-3-*tert.*-butylanthraquinone (0·065 g.), anhydrous sodium acetate (0·5 g.), and a small proportion of cupric acetate were heated under reflux for 2 hours in *o*-dichlorobenzene (5 c.c.). Separation of the products by chromatography then gave 3 : 3′-di-*tert.*-indanthroneazine (0·018 g.) and 3 : 3′-di-*tert.*-butylflavanthrone (0·001 g.) from the red zone containing its precursor.

CLOTHWORKERS RESEARCH LABORATORY,
THE UNIVERSITY, LEEDS.

[*Received, April 15th*, 1952.]

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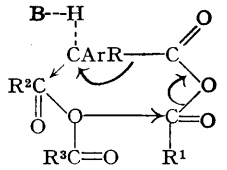
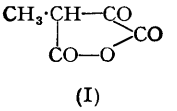
562. *The Conversion of Arylacetic Acids into Ketones.*

By G. L. BUCHANAN and J. MCARDLE.

THE reaction between phenylacetic acid and acetic anhydride in the presence of pyridine was originally described by Dakin and West (*J. Biol. Chem.*, 1928, **78**, 91) who noted that the main product was benzyl methyl ketone. King and McMillan (*J. Amer. Chem. Soc.*, 1951, **73**, 4911) have re-investigated this reaction and shown that dibenzyl ketone is also



$\longrightarrow$ B + CHArR·COR² + CO_2 + R³CO·O·COR¹



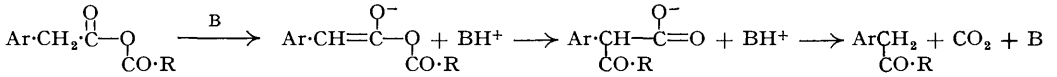
(I)

formed. They consider the reaction to be a "base-catalysed condensation reaction of two acid anhydride molecules," and propose the above mechanism.

We were also engaged on this same problem, and our results are very similar. We agree that the reaction is essentially that of an acid anhydride in the presence of a base, but disagree with the mechanism proposed for these reasons. If the reaction is a condensation reaction as shown above, the essential step is the acylation of the reactive methylene group by a molecule of anhydride. It would therefore be expected that the similarly active methylene group of phenylacetic ester would be acylated under the reaction conditions, yielding ethyl α-phenylacetoacetate. This, we find does not take place. Even the more reactive benzyl cyanide, which would be expected to yield α-acetylbenzyl cyanide, fails to react, and in each case the starting material was recovered in almost quantitative yield. Moreover, such a mechanism assumes that a β-keto-acid anhydride will readily lose carbon

dioxide, although it is known that at least one such substance (I) (Schinz and Hinder, *Helv. Chim. Acta*, 1947, **30**, 1372) is relatively stable.

We envisage a migration mechanism as the only one which satisfactorily accounts for all the facts :



The rearrangement step finds a parallel in the $O \longrightarrow C$ migration of the acyl group in acylated β-keto-esters (Claisen, *Ber.*, 1900, **33**, 3778). It is also possible that the recently reported rearrangement of the enol acetates of ketones (Hauser *et al.*, *J. Amer. Chem. Soc.*, 1950, **72**, 3635) represents a less favourably activated example of the same reaction.

Experimental.—Ethyl phenylacetate (45 g.) was refluxed for 20 hours with acetic anhydride (125 c.c.) and dry pyridine (125 c.c.). The anhydride and pyridine were then removed *in vacuo* and the residual liquid fractionated. The product (43 g.), b. p. 115°/15 mm., gave an amide, m. p. 157° not depressed on admixture of the specimen with an authentic sample of phenylacetamide.

Benzyl cyanide (30 g.) was refluxed for 9 hours with acetic anhydride (100 c.c.) and dry pyridine (100 c.c.), and then worked up as before. The product (27 g.), b. p. 108°/15 mm., gave a benzylidene derivative, m. p. 86°, not depressed on admixture of the specimen with α-cyanostilbene.

THE UNIVERSITY, GLASGOW, W.2. [*Received, April 15th*, 1952.]

563. *Aluminium Hypophosphite.*

By D. A. EVEREST.

THE only previous report in the literature on aluminium hypophosphite was by Rose (*Pogg. Ann.*, 1828, **12**, 86) who obtained a hard amorphous mass by evaporating *in vacuo* a solution of aluminium hydroxide in hypophosphorous acid. No analyses were reported for this material which appeared to be impure.

Aluminium hypophosphite, $Al(H_2PO_2)_3$, has been obtained as an anhydrous crystalline precipitate by heating aluminium hydroxide, or a solution of an aluminium salt, with 50% hypophosphorous acid at 80—90° for 1 hour, the precipitation being rather slow. It was also formed when a solution of an aluminium salt was heated with sodium hypophosphite, precipitation occurring more slowly than with hypophosphorous acid. Aluminium hypophosphite was insoluble in water, in sodium hypophosphite solution, and in hypophosphorous acid. It dissolved in warm sodium hydroxide solution, dilute sulphuric and dilute or concentrated hydrochloric acid; on evaporation of the solution in hydrochloric acid the aluminium hypophosphite was recovered unchanged. No evidence was found for the existence of any double salts between aluminium hypophosphite and aluminium chloride similar to those formed between stannous hypophosphite and stannous chloride or between stannic hypophosphite and stannic chloride (Everest, *J.*, 1952, 2903). When heated, aluminium hypophosphite decomposed, without melting, at approximately 220° with evolution of phosphine and formation of a reddish-brown residue. No conditions were found under which hypophosphorous acid could reduce aluminium compounds to the metal.

Experimental.—Analytical procedures. After dissolution of the sample in 3N-sulphuric acid the aluminium was precipitated with 8-hydroxyquinoline; hypophosphite did not interfere.

Hypophosphite was determined by titrating a solution of the sample in 3N-sulphuric acid with potassium permanganate (Kolthoff, Everest, *loc. cit.*).

Aluminium hypophosphite. The crystalline *salt* obtained as described above was washed with water and absolute alcohol and dried in a vacuum [Found : Al, 12·2; H_2PO_2, 87·4. $Al(H_2PO_2)_3$ requires Al, 12·15; H_2PO_2, 87·85%]. If sodium hypophosphite was substituted for hypophosphorous acid heating had to be continued for about 5 hours to obtain equivalent yields. No conditions were found under which any hydrates were obtained.

BATTERSEA POLYTECHNIC, LONDON, S.W.11. [*Received, April 19th*, 1952.]