# NOTES.

## 865. *Some Complex Organic Salts of Stannous Tin.*

By E. H. Baker and F. C. Tompkins.

The tendency for stannous tin to form complex salts is marked: a series of complex formates having the general formula $M_2Sn(H{\cdot}CO_2)_4,5H_2O$, where M = Na, $NH_4$, or K, were prepared by Elöd and Kolbach (*Z. anorg. Chem.*, 1927, **164**, 297), and a stannous oxyacetate was isolated by Glassman (*Ber.*, 1908, **41**, 36) who showed its constitution to be $Sn_2O(CH_3{\cdot}CO_2)_2$, later confirmed by Elöd and Kolbach (*loc. cit.*). Preparations of complex acetates, however, have not been reported.

During a study of the autoxidation rates of stannous acetate in solution, it was found necessary to investigate the possibility of complex-salt formation in alkali acetate–stannous acetate solutions, and two complex acetates, stannous ammonium acetate and stannous calcium acetate, were isolated.

### Experimental

*Stannous Ammonium Acetate.*—Stannous chloride dihydrate ("AnalaR"; 42 g.) was dissolved in distilled water (200 ml.), and ammonia solution (*d* 0·880) added with stirring until the mixture

was alkaline to phenolphthalein. The stannous hydroxide was filtered off and washed with hot distilled water until free from chloride. It was then refluxed under nitrogen with glacial acetic acid (60 ml.) containing ammonium acetate (14 g.), until completely dissolved. Distillation of the solution was continued until a thick syrup (40 ml.) remained. Benzene (150 ml.) and absolute alcohol (150 ml.) were added, and distillation under nitrogen continued in order to remove most of the residual water. When the volume had been reduced to 150 ml., the flask was cooled at 0° for 1—2 days, whereupon the complex crystallized out. The crystals were filtered off under nitrogen, washed with benzene–alcohol (45—50%) containing glacial acetic acid (5%), and recrystallized from the same solvent. The final product, after being washed with alcohol, then light petroleum (b. p. 40—60°), and dried in a desiccator, was obtained in about 50% yield as colourless prisms, m. p. 138° [Found : C, 25·5; H, 4·4; N, 4·3; Sn, 34·9, 35·0. $NH_4Sn(CH_3{\cdot}CO_2)_3,\frac{1}{2}C_6H_6$ requires C, 25·7; H, 4·3; N, 4·3; Sn, 36·3%].

This *complex* is non-hygroscopic but freely soluble in water with hydrolysis to give a cloudy solution. Clear solutions are obtained in dilute acetic acid or acetic acid–ammonium acetate solution. On dissolution in water, a small quantity of benzene retained from the preparation (see analysis) was released; the benzene was so firmly held that even after a year at room temperature and drying at 60°/10 mm. for 3 hours, an identical analysis was obtained. This firm retention of benzene and its release in aqueous solution suggest the possibility of a clathrate type of compound. The complex is insoluble in benzene itself.

*Stannous Calcium Acetate.*—Calcium acetate (1·7 g.) was dissolved in hot distilled water (15 ml.) at 80°; glacial acetic acid (2 ml.) and stannous acetate solution (10 ml., 1·5M) were added with stirring. The calcium complex, which quickly crystallized from the warm solution, was filtered off under nitrogen. After being washed with alcohol containing a little acetic acid, then light petroleum (b. p. 40—60°), and dried in a desiccator, the product formed colourless, non-hygroscopic leaflets (yield, 70%). It had no definite m. p., but decomposed slowly at about 260° [Found : C, 23·45; H. 3·2; Ca, 6·3; Sn, 37·3. $CaSn_2(CH_3{\cdot}CO_2)_6$ requires C, 22·8; H, 2·85; Ca, 6·35; Sn, 37·6%]. This *complex* was less soluble in water than the ammonium analogue but again hydrolysed giving a cloudy solution. Clear solutions could be obtained in water strongly acidified with acetic acid or in dilute acetic acid containing an excess of calcium acetate.

*Stannous Ammonium Chloroacetate.*—This *compound* was prepared in a similar way : stannous hydroxide (*ex* "AnalaR" $SnCl_2,2H_2O$, 37 g.) was refluxed with 150 ml. of chloroacetic acid (42 g.) to which ammonia (*d* 0·880; 8 ml.) had been added; large colourless prisms, m. p. 187° (decomp.), were obtained on crystallization (yield, *ca.* 80%) [Found : C, 17·5; H, 2·5; N, 3·1; Cl, 25·1; Sn, 28·0. $NH_4Sn(CH_2Cl{\cdot}CO_2)_3$ requires C, 17·3; H, 2·4; N, 3·4; Cl, 25·5; Sn, 28·4%]. In cold water containing sufficient free acid to prevent hydrolysis, this compound was only slightly soluble, thus differing from the analogous acetate.

One of us (E. H. B.) thanks the Tin Research Institute for the award of a grant held during this work.

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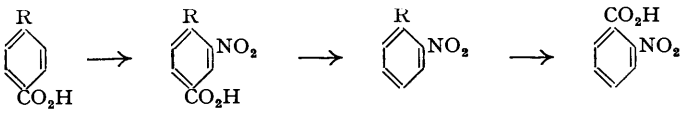
## 866. *The Preparation of Some* 4-n-*Alkyl*-3-*nitrobenzoic Acids.*

By Hussein A. Fahim and Abdallah M. Fleifel.

The *p*-alkylbenzoic acids used as starting material were prepared by alkaline fusion of the corresponding *p*-alkylphenyl methyl ketones at temperatures between 200° and 280°. They were best nitrated by fuming nitric acid alone or by a mixture of concentrated nitric and sulphuric acids. The product was invariably the 4-*n*-alkyl-3-nitrobenzoic acid in which the position of the nitro-group was determined as shown in the scheme :




Experimental.—*Nitration.* (i) The aromatic acid was added gradually to stirred nitric acid (*d* 1·5) at 0°, the mixture being kept at this temperature for 1 hour more, then overnight at room

| Compound | M. p. or b. p./mm. | Crystn. solvent * | Found, %: C | H | N | Formula | Required, %: C | H | N |
|---|---|---|---|---|---|---|---|---|---|
| (a) 4-*Alkyl*-3-*nitrobenzoic acids and derivatives.* | | | | | | | | | |
| 4-Ethyl-3-nitrobenzoic acid | 153—154° † | A | 55·4 | 4·6 | 7·3 | $C_9H_9O_4N$ | 55·4 | 4·6 | 7·2 |
| ,, acid chloride | 242—244°/760 | — | — | — | — | — | — | — | — |
| ,, amide | 110—111 | A | 55·3 | 5·2 | 14·7 | $C_9H_{10}O_3N$ | 55·7 | 5·1 | 14·4 |
| ,, methylamide | 94—95 | ,, | 57·5 | 5·8 | 13·4 | $C_{10}H_{12}O_3N_2$ | 57·7 | 5·8 | 13·4 |
| 3-Nitro-4-*n*-propylbenzoyl chloride | 171—172/8 | — | — | — | — | — | — | — | — |
| ,, amide | 119—120 | A | 57·8 | 5·6 | 13·2 | $C_{10}H_{12}O_3N_2$ | 57·7 | 5·8 | 13·4 |
| ,, methylamide | 68—69 | ,, | 59·4 | 6·4 | 12·4 | $C_{11}H_{14}O_3N_2$ | 59·4 | 6·3 | 12·6 |
| 4-*n*-Butyl-3-nitrobenzoic acid | 138—139 | B | 59·1 | 5·6 | 6·4 | $C_{11}H_{13}O_4N$ | 59·2 | 5·8 | 6·3 |
| ,, acid chloride | 180/7 | — | — | — | — | — | — | — | — |
| ,, amide | 115—116 | A | 59·8 | 6·2 | 12·5 | $C_{11}H_{14}O_3N_2$ | 59·4 | 6·3 | 12·6 |
| ,, methyl amide | 96—97 | ,, | 60·7 | 6·7 | 12·1 | $C_{12}H_{16}O_3N_2$ | 61·0 | 6·8 | 11·9 |
| 4-*n*-Amyl-3-nitrobenzoic acid | 127—128 | B | 60·7 | 6·2 | 5·8 | $C_{12}H_{15}O_4N$ | 60·7 | 6·3 | 5·9 |
| ,, acid chloride | 192—193/20 | — | — | — | — | — | — | — | — |
| ,, amide | 113—114 | A | 61·1 | 6·7 | 11·9 | $C_{12}H_{16}O_3N_2$ | 61·0 | 6·8 | 11·9 |
| ,, methyl amide | 67—68 | ,, | 62·5 | 7·3 | 10·9 | $C_{13}H_{18}O_3N_2$ | 62·4 | 7·2 | 11·2 |
| 4-*n*-Hexyl-3-nitrobenzoic acid | 113—114 | B | 62·2 | 6·7 | 5·6 | $C_{13}H_{17}O_4N$ | 62·1 | 6·8 | 5·6 |
| ,, acid chloride | 187—188/23 | — | — | — | — | — | — | — | — |
| ,, amide | 94·5—95·5 | A | 62·1 | 7·0 | 11·0 | $C_{13}H_{18}O_3N_2$ | 62·4 | 7·2 | 11·2 |
| ,, methyl amide | 56—57 | C | 63·1 | 7·7 | 10·8 | $C_{14}H_{20}O_3N_2$ | 63·6 | 7·6 | 10·6 |
| 4-*n*-Heptyl-3-nitrobenzoic acid | 89—90 | ,, | 63·6 | 7·3 | 5·2 | $C_{14}H_{19}O_4N$ | 63·4 | 7·2 | 5·3 |
| ,, acid chloride | 193—194/12 | — | — | — | — | — | — | — | — |
| ,, amide | 87—88 | A | 63·2 | 7·8 | 10·4 | $C_{14}H_{20}O_3N_2$ | 63·6 | 7·6 | 10·6 |
| ,, methyl amide | 54—55 | B | 65·1 | 7·7 | 9·9 | $C_{15}H_{22}O_3N_2$ | 64·7 | 7·9 | 10·1 |
| 3-Nitro-4-*n*-octylbenzoyl chloride | 204—205/10 | — | — | — | — | — | — | — | — |
| ,, amide | 68—69 | A | 65·2 | 8·0 | 10·3 | $C_{15}H_{22}O_3N_2$ | 64·7 | 7·9 | 10·1 |
| ,, methyl amide | 52—53 | B | 66·4 | 8·5 | 9·8 | $C_{16}H_{24}O_3N_2$ | 65·7 | 8·2 | 9·6 |
| (b) *Derivatives of* 4-n-*alkylbenzoic acids.* | | | | | | | | | |
| 4-*n*-Amylbenzoyl chloride | 144—145/10 | — | — | — | — | — | — | — | — |
| ,, amide | 147—148 | C | 75·5 | 8·9 | 7·0 | $C_{12}H_{17}ON$ | 75·4 | 8·9 | 7·3 |
| ,, methyl amide | 91—92 | A | 76·0 | 9·1 | 6·9 | $C_{13}H_{19}ON$ | 76·1 | 9·3 | 6·8 |
| 4-*n*-Hexylbenzoyl chloride | 176—177/22 | — | — | — | — | — | — | — | — |
| ,, amide | 141—142 | A | 76·2 | 9·4 | 6·5 | $C_{13}H_{19}ON$ | 76·1 | 9·3 | 6·8 |
| ,, methyl amide | 80—81 | C | 76·4 | 9·7 | 6·1 | $C_{14}H_{21}ON$ | 76·7 | 9·6 | 6·4 |
| 4-*n*-Heptylbenzoyl chloride | 195—196/40 | — | — | — | — | — | — | — | — |
| ,, amide | 147—148 | A | 76·5 | 9·7 | 6·1 | $C_{14}H_{21}ON$ | 76·7 | 9·6 | 6·4 |
| ,, methyl amide | 95—96 | ,, | 77·4 | 9·8 | 6·1 | $C_{15}H_{23}ON$ | 77·3 | 9·9 | 6·0 |
| 4-*n*-Octylbenzoyl chloride | 188/12 | — | — | — | — | — | — | — | — |
| ,, amide | 139—140 | D | 77·8 | 10·1 | 6·1 | $C_{15}H_{23}ON$ | 77·3 | 9·9 | 6·0 |
| ,, methyl amide | 84—85 | A | 77·8 | 10·2 | 5·6 | $C_{16}H_{25}ON$ | 77·7 | 10·1 | 5·7 |

* A = benzene–light petroleum; B = light petroleum; C = aqueous ethanol; D = benzene.

† Aschenbrandt, *Annalen*, 1883, **216**, 211, gave m. p. 155—156°.

temperature; the nitro-acid was then precipitated by addition of ice-cold water. (ii) The aromatic acid was added gradually to nitric acid (*d* 1·4) and concentrated sulphuric acid at 5—10°, and the reaction mixture treated as in (i). The 4-alkyl-3-nitrobenzoic acids and some of their derivatives are listed in the Table (section *a*) (p. 4520), and derivatives of 4-*n*-alkylbenzoic acids in section *b*.

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## 867. *The Synthesis of βγ-Unsaturated α-Keto-acids from 1 : 1-Diarylethylenes.*

By FELIX BERGMANN and ABRAHAM KALMUS.

IN Friedel–Crafts reactions of aromatic hydrocarbons with oxalyl chloride the diaryl ketone is the usual product, but 1 : 2-diketones may also be formed (Staudinger, *Ber.*, 1912, **45**, 1596). However, the isolation of an α-keto-acid has not hitherto been reported. Kharasch, Kane, and Brown (*J. Amer. Chem. Soc.*, 1942, **64**, 333) found that the uncatalyzed reaction of 1 : 1-diarylethylenes with oxalyl chloride leads to ββ-diphenylacrylyl chloride (I) with elimination of carbon monoxide and hydrogen chloride. When we followed quantitatively the analogous reaction with 1 : 1-di-*p*-chlorophenylethylene (F. Bergmann *et al.*, *ibid.*, 1948, **70**, 1612), we observed that evolution of carbon monoxide lags considerably behind that of hydrogen chloride. The syrupy reaction mixture was found to contain a small amount of a second acid, m. p. 135—136°. Analysis indicated formula (II; R = H), and the acid was slowly decomposed by boiling oxalyl chloride to ββ-di-*p*-chlorophenylacrylic acid (III).

Independent evidence for the structure of the α-keto-acid (II; R = H) was obtained by condensation of di-*p*-chlorophenylethylene with ethoxalyl chloride at 180°, which gave the ester (II; R = Et) in about 10% yield. The acid obtained by hydrolysis of this ester was identical with the acid, m. p. 135—136°. The keto-ester was characterized by its 2 : 4-dinitrophenylhydrazone and its ultra-violet absorption spectrum (see Table).

*Absorption spectra of ethyl esters of type* (II).

| | Minimum | | Maximum | | Minimum | | Maximum | |
|---|---|---|---|---|---|---|---|---|
| Ethyl ester | λ, Å | log $\epsilon_{mol.}$ | λ, Å | log $\epsilon_{mol.}$ | λ, Å | log $\epsilon_{mol.}$ | λ, Å | log $\epsilon_{mol.}$ |
| 2-Keto-4 : 4-diphenylbut-3-enoate | 2200 | 4·00 | 2300 | 4·02 | 2570 | 3·60 | 3140 | 4·12 |
| 4 : 4-Di-*p*-chlorophenyl-2-ketobut-3-enoate | 2200 | 4·13 | 2320 | 4·21 | 2600 | 3·78 | 3170 | 4·18 |

The reaction proved to be general, and the corresponding keto-ester (and acid) was prepared from 1 : 1-diphenylethylene. Its absorption spectrum resembles very closely that of the dichloro-ester (see Table).

The synthesis and properties of this new class of βγ-unsaturated α-keto-acids are being studied further:

$$CPh_2{:}CH_2 + (COCl)_2 \longrightarrow CPh_2{:}CH{\cdot}COCl\ (I) + CO + HCl$$

$$(p\text{-}Cl{\cdot}C_6H_4)_2C{:}CH_2 + (COCl)_2 \begin{cases} \nearrow (p\text{-}Cl{\cdot}C_6H_4)_2C{:}CH{\cdot}CO{\cdot}CO_2R\ (II) \\ \searrow (p\text{-}Cl{\cdot}C_6H_4)_2C{:}CH{\cdot}CO_2H\ (III) \end{cases}$$

$$(p\text{-}Cl{\cdot}C_6H_4)_2{:}CH_2 + COCl{\cdot}CO_2R \longrightarrow (II)$$

## EXPERIMENTAL

Ethoxalyl chloride (Diels and Nawiasky, *Ber.*, 1904, **37**, 3678; Fourneau and Sabetay, *Bull. Soc. chim.*, 1927, **41**, 537) is conveniently prepared as follows: Ethyl hydrogen oxalate (1 mol.) and thionyl chloride (1·5 mol.) were heated under reflux in an oil-bath at 135°, while dry nitrogen was bubbled through. After 6 hours the mixture was fractionated, and the ester chloride obtained in 90—95% yield, having b. p. 39—40°/18 mm.

*Condensation with* 1 : 1-*Di*-p-*chlorophenylethylene*.—The ethylene (8·3 g.) and ethoxalyl

chloride (9 g., 2 equiv.) were heated to 180° in an oil-bath and kept at 180—190° for 2 hours while dry nitrogen was bubbled through. The brown mass was dissolved in benzene and washed with saturated sodium hydrogen carbonate. Fractionation *in vacuo* gave an oil, b. p. 195—200°/1 mm., which gradually crystallized. From propanol, 1 g. of *ethyl* 4 : 4-*di*-p-*chlorophenyl*-2-*ketobut*-3-*enoate* was obtained in long prismatic columns, m. p. 93—94° (Found : C, 62·2; H, 4·0. $C_{18}H_{14}O_3Cl_2$ requires C, 61·9; H, 4·0%). Hydrolysis at room temperature with 2·5% ethanolic potassium hydroxide and working up as usual gave the free *acid*, and several recrystallizations from benzene–light petroleum gave prismatic rods, m. p. 134—135° (Found : C, 59·8; H, 3·3. $C_{16}H_{10}O_3Cl_2$ requires C, 59·8; H, 3·1%). The ester yielded a 2 : 4-*dinitrophenylhydrazone*, which crystallized from butanol in hexagonal plates, m. p. 202—205° (Found : N, 10·3. $C_{24}H_{18}O_6N_4Cl_2$ requires N, 10·6%).

*Condensation with* 1 : 1-*Diphenylethylene*.—The ethylene (10 g.) and ethoxalyl chloride (15 g.) were heated for 6 hours in an oil-bath at 180—190°. Treatment as above gave a yellow oil, b. p. 177—178°/1 mm., which solidified spontaneoulsy after two redistillations. From light petroleum, 3 g. of *ethyl* 2-*keto*-4 : 4-*diphenylbut*-3-*enoate* were obtained as prisms, m. p. 49—50° (Found : C, 76·9; H, 5·7. $C_{18}H_{16}O_3$ requires C, 77·1; H, 5·7%). The 2 : 4-*dinitrophenylhydrazone* crystallized from butanol in branched prismatic rods, m. p. 180—184° (Found : N, 11·9. $C_{24}H_{20}O_6N_4$ requires N, 12·2%). The corresponding *acid* was obtained as an oil and was purified as follows : it was dissolved in ethanol and an equal volume of water added, whereupon the solution became turbid; when this mixture was heated, most of the turbidity disappeared, and a dark oil separated; after addition of charcoal the mixture was boiled for 1 minute and filtered; the rods, which crystallized upon cooling, were purified from ligroin, forming long needles, m. p. 125° (Found : C, 76·5; H, 5·2. $C_{16}H_{12}O_3$ requires C, 76·2; H, 4·8%).

*Isolation of* 4 : 4-*Di*-p-*chlorophenyl*-2-*ketobut*-3-*enoic Acid from the Reaction with Oxalyl Chloride*.—The ethylene (8 g.) and oxalyl chloride (15 g.) were kept at 30° for 1 week. The excess of chloride was removed *in vacuo*, and the residue mixed with excess of 10% sodium hydroxide solution. After 6 hours at room temperature the mixture was boiled with charcoal and filtered hot. The sodium salts, which crystallized on cooling, were removed and added to ice-cold hydrochloric acid. The crude acid (10 g.) melted at about 70°. It was dissolved in dilute acetic acid and left in a Dewar flask for over a month. The crystals were of two forms—long needles and clumps. The rather small amount of needles was separated mechanically and recrystallized first from dilute methanol (needles), then twice from benzene–light petroleum, forming prismatic rods, m. p. 135—136° undepressed on admixture with the acid (II; R = H) above. The clumps were recrystallized from dilute acetic acid, then from benzene–light petroleum; this compound, m. p. 175°, is identical with ββ-di-*p*-chlorophenylacrylic acid (cf. F. Bergmann *et al.*, *loc. cit.*).

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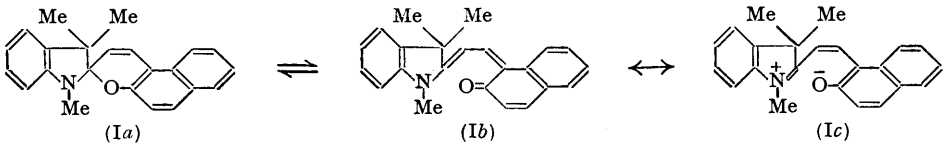
## 868. *Formation of Coloured Forms of Spirans by Low-temperature Irradiation.*

By ERNST FISCHER and YEHUDA HIRSHBERG.

IT has been reported (Hirshberg, *Compt. rend.*, 1950, **72**, 5009) that certain derivatives of dianthronyl are reversibly converted into coloured modifications by irradiation at low temperatures. Similar observations with certain spirans are now reported. Several spirans exist in solution in thermal equilibrium with coloured modifications, the concentration of the latter increasing with temperature (see Koelsch, *J. Org. Chem.*, 1951, **16**, 1362, and Knott, *J.*, 1951, 3038, where previous literature is listed). Chaudé and Rumpf (*Compt. rend.*, 1951, **233**, 405) found from the plots of the logarithm of the molar extinction coefficients against the reciprocal of the absolute temperature, for a series of such compounds, that the heats of conversion into the coloured modification were 2—6 kcal./mole. By assuming that at infinite temperature this conversion is virtually complete, they estimated the molar extinction coefficient of the pure coloured form by extrapolation to $1/T = 0$.

The coloured modifications are generally believed to be resonance hybrids of quinoid and bipolar forms (Koelsch, *loc. cit.*; Knott, *loc. cit.*). Thus, for 1 : 3 : 3-trimethylindoline-

2-*spiro*-6′-(2′ : 3′-β-naphthopyran) (I), solutions of which become pink when heated, equilibrium with a hybrid of (I*b*) and (I*c*) has been postulated (Bergmann, Weizmann, and Fischer, *J. Amer. Chem. Soc.*, 1950, **72**, 5009).




(I*a*) (I*b*) (I*c*)

When solutions of (I) are irradiated for about a minute at below −50°, they become intense violet-red. No such effect is observed with the solid compound, but in supercooled solutions in ethanol–methanol coloration occurs to some extent even at liquid-air

FIG. 1. *Absorption spectra for spiran* (I) : (*a*) *at low temperature*; (*b*) *at* 25°; (*c*) *at* 135°.

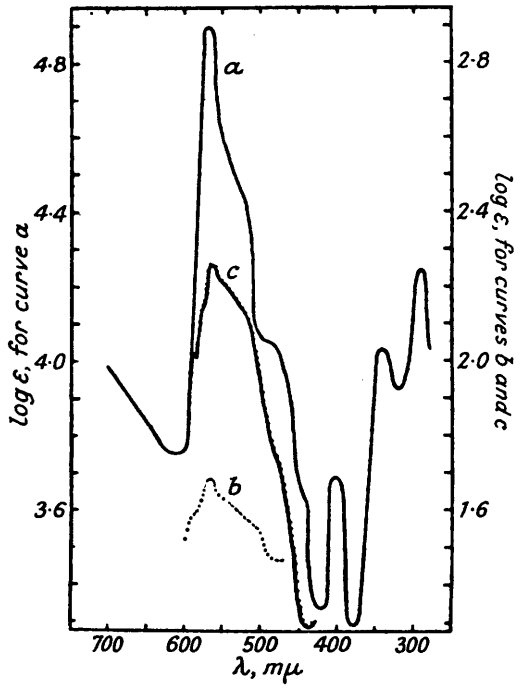
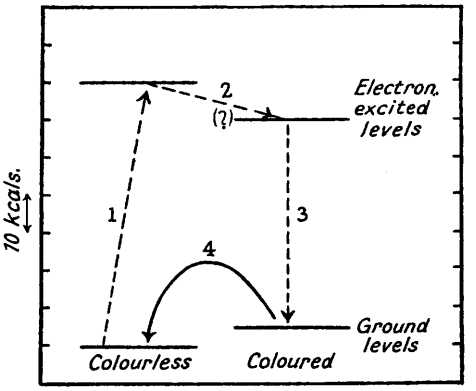



FIG. 2. *Schematic representation of photoconversion* (*steps* 1, 2, 3) *and thermal reversion* (*step* 4). *The thermal conversion into the coloured form proceeds by the reverse of step* 4.



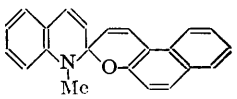
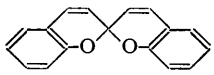

temperature. Fig. 1, curve *a*, represents the absorption spectrum at −100° of a solution irradiated at this temperature to maximum absorption intensity. Curves *b* and *c* give the absorption spectra of solutions at 25° and 135°. The similarity between the temperature-dependent absorption band in *b* and *c* and the corresponding band in *a* is evident.

The molar extinction coefficient of the irradiated solution at the maximum (about 570 mμ) is approximately 88,000, in good agreement with the value of 100,000 estimated by Chaudé and Rumpf (*loc. cit.*) for the coloured species. It therefore appears plausible that the coloured modifications formed by either heat or low-temperature irradiation are identical, and that in the latter process practically complete conversion into the coloured form takes place.

On storage, the irradiated solution loses its colour at a rate dependent on temperature, and the cycle is indefinitely reversible. The rate of this reverse reaction was measured at several temperatures between −30° and −50°. By assuming the reaction to be of the first order, its critical increment was estimated graphically [the plot of log (reversion time) against $1/T$ was linear]; the resulting value, $15 \pm 2$ kcal./mole, may be regarded as a minimum for the potential barrier between the coloured and the colourless form; the

actual activation energy for such a complex molecule may be considerably higher. The frequency factor calculated from the above observations is about $10^{12\cdot5}$.

If the coloured form is a resonance hybrid of (I*b*) and (I*c*), one would expect the low-temperature irradiation to cause a considerable increase in the dielectric constant of the solution. It is noteworthy that the structurally similar (II) possesses a temperature-independent absorption maximum at 600 mμ ($\varepsilon = 45{,}000$) (Chaudé and Rumpf, *loc. cit.*) and

(II)   (III)

a dipole moment of about 10 D (Bergmann *et al.*, *loc. cit.*). The latter authors have therefore suggested that conversion of this compound into a hybrid, analogous to (I*b*) ⟷ (I*c*), is complete even at room temperature.

The dielectric constants of heptane and toluene solutions of (I) were measured at −78°, before and after irradiation at this temperature. By analogy with (II), the dielectric constant of these solutions should increase by about 0·09 units on irradiation. However, no increase in dielectric constant was observed, within the experimental error of 0·0005 unit.*

No colour develops on heating solutions of the colourless spiran (III) (Koelsch, *loc. cit.*), but when such solutions are irradiated at low temperatures, an intense blue colour is produced. From the rates of the disappearance of colour at several temperatures a critical increment of 17·5 kcal./mole and a frequency factor of $10^{14\cdot5}$ were determined graphically. [The absorption curve has a broad maximum at 670 (log ε 4·39), and a narrow one at 470 mμ (log ε 4·16).]

The photoconversion of (I) and (III) into coloured forms does not occur with light of wave-lengths greater than about 540 mμ (*i.e.* energies lower than about 65 kcal./mole). The fluorescence spectra of the two modifications of (I) were measured in supercooled solutions at −180°, the 365-mμ mercury line being used as light source. A considerable enhancement of the fluorescence of the coloured form and a bathochromic shift of its maximum (from 600 to 615 mμ) were observed.

The following tentative conclusions may be drawn : (*a*) The (thermal) reaction, coloured ⟶ colourless form, requires the passing of potential barriers of at least 15 kcal./mole, indicating that configurational changes in the molecules (I) are involved. (*b*) The low-temperature photoconversion into the coloured form involves a transition between excited electronic states of the two modifications, followed by a " freezing-in " of the coloured form. The postulated steps involved in the photoconversion and the thermal reversion over a potential barrier are presented schematically in Fig. 2. (*c*) Non-thermochromic spirans [*e.g.* (III)] also exist in coloured modifications; it is probable that the energy difference between the two modifications is so large that no observable shift of the thermal equilibrium towards the coloured form can occur within the accessible temperature range. This increased energy difference does not affect the photoconversion which proceeds by a different mechanism, and is independent of the thermal equilibrium. (*d*) Bipolar mesomers do not contribute materially to the structure of the coloured modifications described.

We are grateful to Dr. Anna Weizmann for samples of compounds (I) and (III).

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* In a previous communication (Bergmann *et al.*, *loc. cit.*) it was reported that the dipole moment of (I) at 90° is not significantly larger than that at 30°. However, these results were inconclusive, since at this temperature only a small percentage of the substance exists in the coloured modification.

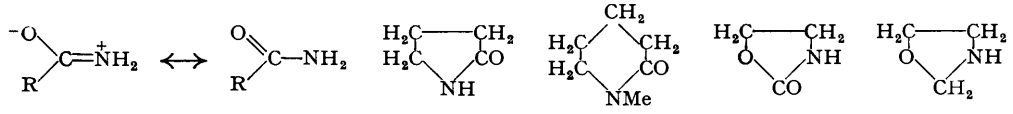
## 869. *Electric Moments and Intermolecular Hydrogen Bonds of Cyclic Amides and Oxazolidones.*

By Ernst Fischer.

The contribution of bipolar mesomers (I) to the structure of acid amides (II) has been estimated from a comparison of the observed electric moments with those calculated from bond moments or from the moments of simpler molecules (see Bates and Hobbs, *J. Amer. Chem. Soc.*, 1951, **73**, 2151, where previous literature is listed).

Because of the non-planarity of the nitrogen valencies, and the possible rotation about the carbon–nitrogen bond in (II), calculations of the moment of (II) from bond moments must be based on some assumption with regard to the configuration of (II) in solution. Such assumptions are generally not unambiguous, and as a result some controversy has recently arisen with regard to the significance of the conclusions reached (Kumler, *ibid.*, 1952, **74**, 261).

The configuration of cyclic amides, such as pyrrolid-2-one (III), is free from these ambiguities, and their moments can therefore be estimated from bond moments with a reasonable degree of accuracy. Comparison with the experimental moments may then lead to more conclusive results with regard to the contribution of bipolar mesomers. The experimental moments of 2·9 D for *cyclo*pentanone (Gunthard and Gaumann, *Helv. Chim. Acta*, 1951, **34**, 39) and 1·6 D for pyrrolidine (Robles, *Rec. Trav. chim.*, 1939, **58**, 111) permit calculation of the moment for the planar model of (III) as about 3·9 D, the value assumed for the angle between the N–H valency and the ring plane scarcely affecting this figure. Unfortunately no reliable experimental figures are available for (III). For 1-methylpiperid-2-one (IV) in benzene solution a moment of 4·0 D was found (Syrkin and Shott-Levova, *Acta Physicochim. U.R.S.S.*, 1945, **20**, 397) which would correspond to a value of about 4·2 D for the non-methylated piperid-2-one. Since the relative position of the polar bonds in this molecule will not differ much from that in (III), this figure may be compared with the "theoretical" value of 3·9 D. If the difference (0·3 D) is ascribed to the contribution of bipolar mesomers analogous to (I), this contribution would amount to about 5%.



(I) (II) (III) (IV) (V) (VI)

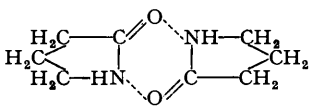
Analogously, the moment of the planar, pentagonal model of oxazolid-2-one (V) would be about 4·1 D, based on the experimental moments of 1·6 D for oxazolidine (VI) (Bergmann, Fischer, Zimkin, and Pinchas, *Rec. Trav. chim.*, 1952, **71**, 213) and 2·9 D for *cyclo*pentanone. For 1-methyloxazolid-2-one in benzene solution a moment of 5·04±0·05 D was found; the same value was observed for extremely dilute solutions (see below) of oxazolid-2-one itself. From the difference of about 1 D between the calculated and the observed moment, a contribution of about 16% from bipolar mesomers analogous to (I) is calculated for (V).

Amides tend to associate in benzene solutions, the predominant product in dilute solutions ($\chi < 0{\cdot}005$) being the ring dimer (VII), in which the two molecules are held together mainly by two hydrogen bonds.* Hobbs and Bates (*J. Amer. Chem. Soc.*, 1952, **74**, 746) have recently estimated the corresponding dimerisation constants from the deviations from linearity of the curves of dielectric constant increment ($\Delta\varepsilon$) *versus* concentration.

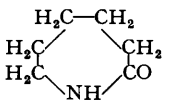
The present measurements show that for oxazolidone this association is very much more pronounced. In the Figure values of $\Delta\varepsilon$ of benzene solutions are recorded at weight fractions up to about 0·008, for oxazolidone (V), 1-methyloxazolid-2-one and 6-amino-

* Mizushima, Simanouti, Nagakura, Kuratani Tsuboi, Baba, and Fujioka (*J. Amer. Chem. Soc.*, 1950, **72**, 3490) found that in carbon tetrachloride solutions of *N*-methylacetamide, unlike those of the amides of types (II) and (III), association takes place to give chains rather than rings.

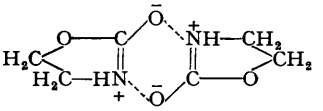
hexanoic lactam (VIII), the latter serving as a representative cyclic amide. It is evident from a comparison of the three curves (*a*) that the deviation from linearity of the curve is much larger for (V) than for (VIII) and (*b*) that no such deviation occurs when the *N*-hydrogen atom is replaced by methyl. It follows from these observations that association



(VII)



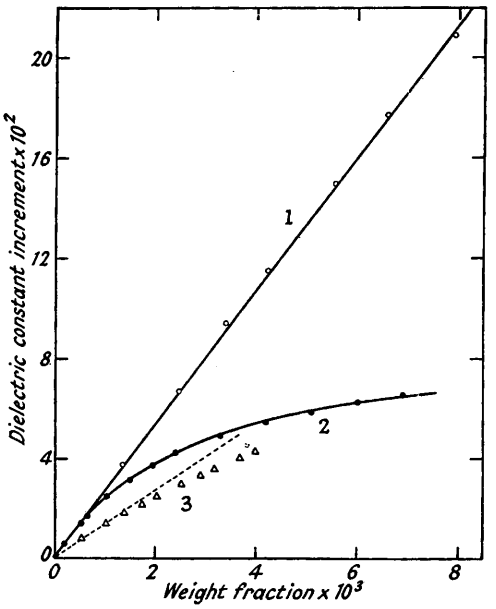
(VIII)



(IX)

in this range of concentration is due mainly to the formation of intermolecular hydrogen bonds and that this type of association is much more pronounced in solutions of oxazolidone than in cyclic amides.

It thus appears that for compounds containing the amide group the tendency to formation of intermolecular hydrogen bonds runs parallel with the contribution of bipolar mesomers




*Dielectric constant increments of benzene solutions at* 30°.

1, 1-*Methyloxazolid-2-one.*
2, *Oxazolid-2-one.*
3, 6-*Aminohexanoic lactam.*

to the structure of these compounds. A plausible explanation may be that the van der Waals forces operative in the formation of hydrogen bonds between simple amides are augmented in oxazolid-2-one by electrostatic attraction forces between the negative oxygen and the hydrogen atom, to which the positive charge of the nitrogen atom is probably transferred (IX) (cf. Syrkin and Diatkina, " Structure of Molecules and the Chemical Bond," Butterworth Scientific Publ., London, 1950, pp. 274—275).

## Experimental

1-*Methyloxazolid-2-one* (D. Ben-Ishai, unpublished results).—This was synthesised from 2-hydroxyethylmethylamine according to Katchalski and Ben-Ishai (*J. Org. Chem.*, 1950, **15**, 1067). The colourless oily *lactam* distilled at 86—88°/3 mm. and had $n_D^{25}$ 1·454 and $d_4^{25}$ 1·170 (Found : C, 47·4; H, 7·4; N, 13·9. $C_4H_7O_2N$ requires C, 47·5; H, 7·0; N, 13·85%). The molar refraction was $R_D$ 23·4 ml. From bond refractions (Vogel, Cresswell, Jeffery, and Leicester, *J.*, 1952, 514) a value of 24·1 ml. is calculated. Similar negative values for $R_D$ (obs.) $-R_D$ (calc.) have been reported for other five-membered heterocyclic compounds (Bergmann *et al.*, *loc cit.*).

*Oxazolid-2-one.*—This was prepared and purified according to Katchalski and Ben-Ishai (*loc. cit.*) and had m. p. 89—90°.

6-*Aminohexanoic Lactam.*—A commercial product was recrystallized several times from heptane. The colourless leaves had m. p. 65—66°.

The measurement of densities and dielectric constants, as well as the calculation of the dipole moments from the slope of the linear plots of these quantities *versus* weight fraction, have been described elsewhere (Fischer, *J. Chem. Physics*, 1951, **19**, 395).

Dipole moments were calculated from results of measurements at weight fractions below 0·0005.

A rough calculation shows that in a 0·6% (by wt.) solution of oxazolidone in benzene about 70% of the solute is dimerized. No attempt has been made to determine the dimerisation constant accurately at these high degrees of association.

The author thanks Dr. E. D. Bergmann for his interest, and Dr. Dov Ben-Ishai for samples of oxazolidones.

THE WEIZMANN INSTITUTE OF SCIENCE, REHOVOTH, ISRAEL. [*Received, June 18th*, 1952.]

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## 870. *Assay and Degradation of* $^{14}$C-*Labelled Choline.*

By H. R. V. ARNSTEIN.

DURING work on the biosynthesis of choline from $^{14}$C-labelled precursors by the rat, the amount of $^{14}$C in the methyl groups and ethanolamine moiety of choline had to be estimated separately. For this purpose choline chloroplatinate is usually oxidised with alkaline permanganate to trimethylamine, which is isolated as the chloroplatinate (du Vigneaud, Cohn, Chandler, Schenk, and Simmonds, *J. Biol. Chem.*, 1941, **140**, 625). The radioactivity in the trimethylamine chloroplatinate should correspond with the amount of $^{14}$C in the methyl groups of choline and the radioactivity in the ethanolamine moiety can then be calculated by difference.

However, in some experiments, particularly when the choline solution was heated vigorously during the permanganate oxidation, inconsistent results were obtained and the degradation procedure was therefore checked with synthetic choline labelled with $^{14}$C in the methyl groups. It was again found that the radioactivity of the " trimethylamine " chloroplatinate was variable and in one experiment was only 16% of the calculated value. This chloroplatinate sample was converted into the free base which was analysed by vapour-phase partition chromatography (James, Martin, and Smith, *Biochem. J.*, 1952, **52**, 238), kindly carried out by Dr. A. T. James. It was found that the supposed trimethylamine consisted of ammonia 86% and trimethylamine only 14%, the latter value being in good agreement with the observed radioactivity of the chloroplatinate. It is also of interest that the mixture appeared to contain neither mono- nor di-methylamine.

In further experiments the " trimethylamine " chloroplatinate fraction was converted into barium carbonate by wet combustion (cf. Van Slyke and Folch, *J. Biol. Chem.*, 1940, **136**, 509) and the radioactivity of the choline-methyl groups was calculated from the radioactivity of the barium carbonate.

*Radioactivity of synthetic* $^{14}$C-*methyl-labelled choline and degradation products.*

| Compound | Radioactivity (μc/mole) * Exp. I | Exp. II |
|---|---|---|
| Choline chloroplatinate | 4·2 | 2·8 |
| " Trimethylamine " chloroplatinate | 2·8 | 2·4 |
| $BaCO_3$ obtained by wet combustion of " trimethylamine " chloroplatinate | 0·73 | 0·48 |
| Methyl groups of choline (calc. from radioactivity of $BaCO_3$) | 4·4 | 2·8 |

* Standard error ±3%.

The Table shows that there is good agreement between the observed radioactivity of the choline chloroplatinate and the value calculated from the barium carbonate derived from the " trimethylamine " chloroplatinate and it is suggested that combustion of the " trimethylamine " is essential for reliable results.

For the assay of choline itself, however, the wet combustion procedure of Van Slyke and Folch (*loc. cit.*) was found to be unsatisfactory. When synthetic $^{14}$C-methyl-labelled

choline (specific activity : 650 μc per g. of carbon) was oxidised by this method, the carbon dioxide, isolated as barium carbonate, contained only 52% of the theoretical radioactivity (340 μc per g. of C, here and in all cases). As difficulties in obtaining complete combustion of, for example, the xanthhydryl derivative of urea have been reported (Armstrong, Singer, Zbarsky, and Dunshee, *Science*, 1950, **112**, 531), it seemed likely that the above result was due to the incomplete combustion of the methyl groups of choline. This was confirmed by oxidising choline labelled with $^{14}C$ in the ethanolamine moiety and collecting the carbon dioxide in fractions. The specific radioactivity of the choline chloroplatinate was 3·4 μc per g. of carbon, which was unchanged after conversion into the mercuric chloride complex (3·52 μc). The specific radioactivities of the first two fractions of carbon dioxide from the wet combustion of this material were 5·9 and 5·8 μc respectively. Carbon dioxide evolution then ceased and a further quantity of fresh oxidation mixture had to be added. The carbon dioxide which was then evolved had a specific radioactivity of 0·75 μc.

It is obvious from the above results that complete combustion of the sample is essential for accurate radioactivity estimations of $^{14}C$-labelled choline as barium carbonate and it is more convenient to measure the radioactivity of the chloroplatinate directly.

## Experimental

*Radioactivity Determinations.*—The measurements were carried out on " infinite thickness " samples, *i.e.*, 25 mg. or more of material per sq. cm., mounted on 1-sq. cm." Polythene " discs, as described by Popják (*Biochem. J.*, 1950, **46**, 560). Samples were counted with a helium-filled bell-shaped Geiger–Müller counter which had a thin mica window. The " background " of the instrument was about 8 counts/min. and a sample which contained 1 μc of $^{14}C$ per g. of substance gave aprox. 1000 counts/min. when counted as described above.

*Preparation of Choline Chloride Labelled with $^{14}C$ in the Ethanolamine Moiety.*—The synthesis of this compound from $^{14}CH_3 \cdot CO_2Na$ (obtained from the Radiochemical Centre, Amersham) has already been described (Arnstein, *Biochem. J.*, 1951, **48**, 27). The choline contained no $^{14}C$ in the carbinol-carbon atom (D. B. Sprinson, private communication) and the reaction of trimethylamine with ethylene chlorohydrin therefore does not involve the intermediary formation of ethylene oxide. The choline was assayed both as the chloroplatinate (3·4 μc per g. of carbon) and the mercuric chloride complex (3·5 μc).

*Preparation of [$^{14}C$-methyl]Choline Chloride.*—[$^{14}C$-methyl]Choline iodide, prepared by the reaction of $^{14}CH_3I$ with dimethylaminoethanol essentially as described by Roe (*Elisha Mitchell Sci. Soc.*, 1951, **67**, 54) was dissolved in water and converted into the chloride by addition of excess of aqueous silver acetate, followed by excess of 2N-hydrochloric acid. The silver halides were removed by centrifuging and the solution of choline chloride was evaporated to dryness *in vacuo*. For assay, this material was converted into the chloroplatinate.

*Wet Combustion of Samples.*—Approx. 30—50 mg. of choline chloroplatinate (6—10 mg. of C) were heated with the oxidation mixture (2—5 ml.) described by Van Slyke and Folch (*loc. cit.*) in a tube through which carbon dioxide-free nitrogen was slowly passed. The exit gases were bubbled through approx. 10—20 ml. of saturated barium hydroxide solution. The barium carbonate was collected, washed twice with carbon dioxide-free distilled water, twice with ethanol, and once with ether, and dried at 100°.

*Oxidation of Choline to Trimethylamine.*—Choline chloroplatinate was oxidised with alkaline potassium permanganate as described by du Vigneaud *et al.* (*loc. cit.*; cf. Lintzel and Monasterio, *Biochem. Z.*, 1931, **241**, 273) in a flask through which carbon dioxide was passed, the alkaline solution of choline being warmed to about 60—100° before the permanganate was added. The trimethylamine was absorbed in two traps which contained 0·3N-hydrochloric acid. The hydrochloric acid was evaporated *in vacuo*. The residue was dissolved in ethanol, and a solution of chloroplatinic acid in ethanol was added. The trimethylamine chloroplatinate was collected, washed with alcohol and ether, and dried at 100°.

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## 871. *The Preferential Reduction of Nitro-groups in Polynitro-compounds. Part V.** 1 : 3 : 6-, 1 : 3 : 8-, *and* 1 : 4 : 5-*Trinitronaphthalene.*

By E. R. Ward and L. A. Day.

Previous work in this field (Hodgson *et al.*, Part I, *J.*, 1943, 318; Part II, *J.*, 1945, 454; Part IV, *J.*, 1945, 794; cf. *J.*, 1949, 1187) has shown that preferential reduction of polynitronaphthalenes occurs at α-positions with acid stannous chloride and at β-positions with alkaline sulphides. The production of 4 : 5-dinitro-2-naphthylamine from 1 : 3 : 8-trinitronaphthalene with sodium hydrogen sulphide and 3 : 6-dinitro-1 : 8-naphthylenediamine from 1 : 3 : 6 : 8-tetranitronaphthalene with acid stannous chloride did not, however, have the same significance as reductions of the dinitronaphthalenes since these reaction products represented considerably less than half of the starting materials. Working under similar reaction conditions we have now investigated the reduction of 1 : 3 : 6-, 1 : 3 : 8-, and 1 : 4 : 5-trinitronaphthalenes.

By reaction with acid stannous chloride 1 : 3 : 6-trinitronaphthalene affords a 25% yield of the expected 3 : 6-dinitro-1-naphthylamine, the latter being orientated by deamination to the known 2 : 7-dinitronaphthalene. Despite considerable variation in procedure only very small amounts of amine could be isolated in reductions of this compound with sodium hydrogen sulphide, the main reaction appearing to be replacement of one or more nitro-groups by sulphur-containing radicals. The yield of basic product was insufficient to merit further investigation, and in any case the result would be of little theoretical significance.

Unsuccessful attempts to reduce 1 : 3 : 8-trinitronaphthalene with acid stannous chloride have already been reported (Ward, Thesis, London Univ., 1946) and further attempts have failed to produce a significant amount of reduction product capable of purification.

With stannous chloride 1 : 4 : 5-trinitronaphthalene gave a very small yield of what appeared to be a mixture of two amines, and with sodium hydrogen sulphide gave a very small yield of an amine not identical with 4 : 8-dinitro-1-naphthylamine. The main product in the latter case appeared to be sodium 4 : 8-dinitro-1-naphthyl sulphide, this being confirmed by its reaction with *o*-dinitrobenzene to give a compound identical with that given by the reaction of sodium *o*-nitrothiophenoxide with 1 : 4 : 5-trinitronaphthalene. Both sulphides are presumably 4 : 8-dinitro-1-*o*-nitrophenylthionaphthalene on analogy with the product arising from 1 : 4 : 5-trinitronaphthalene and sodium *o*-nitrothiophenoxide (Hodgson and Ward, *J.*, 1948, 2017). As expected neither 1 : 3 : 6- nor 1 : 3 : 8-trinitronaphthalene would react with sodium *o*-nitrothiophenoxide.

It is convenient to report here that 1 : 4 : 5 : 8-tetranitronaphthalene in reaction with this reagent afforded a compound which is probably 4 : 8-dinitro-1 : 5-di-*o*-nitrophenylthionaphthalene, simultaneous replacement of two mobile nitro-groups occurring.

### Experimental.

Analyses are by Drs. Weiler and Strauss, Oxford.

*Reductions with Stannous Chloride.*—The trinitronaphthalene (10 g.), suspended in acetic acid (40 c.c.), was treated, with stirring, with a solution of hydrated stannous chloride (25 g.) in acetic acid (60 c.c.) saturated with dry hydrochloric acid. The rate of addition was such as to keep the temperature at 25—30° (*ca.* 30 minutes). The mixture was stirred for a further 30 minutes and then as much acetic acid as possible (*ca.* 70—80 c.c.) removed by distillation *in vacuo*. The residue was poured on ice and basified with aqueous sodium hydroxide (20%). The crude product was extracted with warm dilute hydrochloric acid and reprecipitated with ammonia at 0°.

1 : 3 : 6-Trinitronaphthalene gave 3 : 6-*dinitro*-1-*naphthylamine* (2·2 g., 25%), red-orange needles, m. p. 270—272°, from ethanol (Found : N, 18·4. $C_{10}H_7O_4N_3$ requires N, 18·0%).

1 : 4 : 5-Trinitronaphthalene gave a mixture of red and yellow needles, m. p. 130—140° (0·2 g.), not separated by crystallisation from ethanol; a large amount of black tar was also obtained.

* Part IV, *J.*, 1945, 794.

*Orientation of* 3 : 6-*Dinitro*-1-*naphthylamine.*—The amine (1 g.), dissolved in sulphuric acid (5 c.c.; *d* 1·84), was stirred into a solution of sodium nitrate (0·4 g.) in sulphuric acid (2 c.c.; *d* 1·84). The mixture was then added slowly to acetic acid (14 c.c.) below 20°. After 30 minutes the diazonium solution was added rapidly to methanol (50 c.c.) containing suspended cuprous oxide (5 g.). After 15 minutes' stirring the mixture was poured into ice-water (100 c.c.), and the solids were filtered off, washed with water, and extracted portionwise with hot ethanol (100 c.c. in all). The extract on concentration deposited 2 : 7-dinitronaphthalene, which, recrystallised from ethanol, had m. p. 232° alone or admixed with an authentic specimen.

*Reductions with Sodium Hydrogen Sulphide.*—The trinitronaphthalene (2 g.) was suspended in methanol (30 c.c.) with sodium hydrogen carbonate (0·4 g.) and reduced by the addition of aqueous methanolic sodium hydrogen sulphide (Hodgson and Ward, *J.*, 1948, 242; 1·5 mols.) during 15 minutes. Reaction was continued a further 15 minutes, the mixture added to ice-water (150 c.c.), and the solid separated, washed with water, and extracted with warm dilute hydrochloric acid. The extracts were basified at 0° with ammonia.

1 : 3 : 6-Trinitronaphthalene gave only a very small amount of yellow-brown amine on basification, the reaction liquors on acidification giving a black tar which could not be purified. 1 : 4 : 5-Trinitronaphthalene gave a small amount of an orange amine (0·1 g.), which, crystallised from ethanol, had m. p. 180—190° (mixed m. p. with 4 : 8-dinitro-1-naphthylamine 140°). The reaction liquor gave a grey precipitate on acidification. This was dissolved in methanol (5 c.c.) containing sodium hydroxide (0·1 g.), and the solution filtered to remove tar and added dropwise to a solution of *o*-dinitrobenzene (1 g.) in methanol (5 c.c.) under reflux. After 10 minutes the mixture was cooled and the black reaction product separated. Recrystallised from acetic acid (charcoal) it had m. p. 190° unchanged by admixture with 4 : 8-dinitro-1-*o*-nitrophenylthionaphthalene. Variations of procedure with these trinitronaphthalenes, *e.g.*, reaction at room temperature over long periods, altering the amount of sodium hydrogen carbonate, using other sulphides of sodium, failed to improve the yields of amines.

*Reaction of Polynitronaphthalenes with Sodium* o-*Nitrothiophenoxide.*—1 : 4 : 5-Trinitronapthalene (0·5 g.) suspended in ethanol (20 c.c.) was treated with *o*-nitrothiophenol (0·3 g.) and sodium hydroxide (0·1 g.) in ethanol (1·5 c.c.) After 10 minutes' refluxing the mixture was cooled and the solid 4 : 8-*dinitro*-1-*o*-*nitrophenylthionaphthalene* (0·3 g.) filtered off. Recrystallised from acetone, then from acetic acid, this had m. p. 190° (Found : S, 8·2. $C_{16}H_9O_6N_3S$ requires S, 8·6%).

Under similar reaction conditions 1 : 3 : 6-, and 1 : 3 : 8-trinitronaphthalenes gave no solid reaction product and the reaction mixture contained no liberated nitrite.

4 : 8-*Dinitro*-1 : 5-*di*-o-*nitrophenylthionaphthalene.* 1 : 4 : 5 : 8-Tetranitronaphthalene (0·5 g.), suspended in ethanol (20 c.c.) similarly treated, gave 4 : 8-*dinitro*-1 : 5-*di*-o-*nitrophenylthionaphthalene* (0·5 g.), m. p. 305—307° (from acetic acid) (Found: N, 10·7; S, 12·2. $C_{22}H_{12}O_8N_4S_2$ requires N, 10·6; S, 12·2%).

The authors thank the Department of Scientific and Industrial Research for a maintenance grant to one of them (L. A. D.) and Imperial Chemical Industries Limited, Dyestuffs Division, for gifts of chemicals.

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## 872. *The Rate of Nucleation of Ammonium Iodide on Mica.*

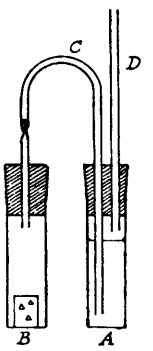
By R. S. BRADLEY.

THE ideal method of studying two-dimensional nucleation and crystal growth would be to prepare a large perfect crystal surface and to study at what degree of supersaturation growth proceeds. This is not normally possible, since the large crystals have grown in all probability by Frank's dislocation mechanism (*Phil. Mag. Suppl.*, 1952, **1**, 91), and no surface nucleation of the classical type required for a perfect surface will be necessary. It was hoped to overcome this difficulty by growing ammonium iodide on a mica substrate, comparatively large patches of which are molecularly perfect although there are many steps (Tolansky, " Multiple beam interferometry of surfaces and films," Oxford Univ.

Press, 1948) and occasional points of emergence of dislocation vectors (Amelinckx, *Nature*, 1952, **169**, 580).

## Experimental

Ammonium iodide grows with the 111 face parallel to the mica and appears as oriented prisms (Friedel, " Leçons de cristallographie," Paris, 1926). The apparatus used to detect the appearance of these prisms consisted of two specimen tubes *A* and *B*, 1 cm. in diameter (Figure) with thin glass walls. *A* and *B* were fitted with rubber bungs and were joined by a glass tube C in which there was a constriction holding a small pellet of compressed filter paper. Tube *A* was filled with a hot saturated solution of ammonium iodide, and after the apparatus had been assembled with a piece of freshly cleaved mica in *B* the tubes were immersed in a thermostat at 30—50°, with the narrow tube *D* emerging from the thermostat liquid surface. The hot solution of ammonium iodide was cooled and rapidly attained equilibrium. After the apparatus had remained in the thermostat for an hour, with constant shaking, tube *D* was attached to a filter pump, and air was removed from *A* and *B*. On the release of the pump the saturated solution was forced into *B* and was filtered from micro-crystals and particulate matter. The apparatus was raised until the rubber bungs just protruded from the thermostat liquid, water was wiped off, and tube *B* was removed and closed by a stopper carrying a solid glass rod for convenience of clamping. Tube *B* was then plunged, still stoppered, into water at 60—70°, in order to destroy any micro-crystalline nuclei which had escaped filtration, and after 30 minutes was replaced in the thermostat. The latter was then allowed to cool at approx. 1° per hour, and the mica was observed with a lens for the appearance of crystals of ammonium iodide. No significant difference was observed in the results when the rate of cooling was greatly decreased. The temperature of appearance of the crystals was surprisingly sharp and very small crystals could easily be detected by the glinting in the light of a lamp. In so far as the crystals had reached visible size before their appearance was recorded a slight overshooting of the super-cooling for nucleation was inevitable, but as judged by the extent to which the crystals grew on further slow cooling and the results with different rates of cooling the overshooting was only of the order 0·1°. A batch of five sets were studied at one time and the whole was repeated many times.




Ammonium iodide solutions decompose slowly, giving small quantities of iodine, but no significant difference was noted between the critical degree of cooling for the crystallisation of brown and colourless solutions. The filter did not appreciably alter the concentration, as was proved by filtering the solution as above and then adding a few mg. of ammonium iodide to the filtrate. Even after the solution had been shaken for an hour in the thermostat the crystal grains had neither grown nor dissolved; since the ammonium iodide dissolved amounted to a few grams, this is a sensitive test. It seemed unlikely that vibration was influencing the rate of crystal nucleation, since the supersaturated solutions deposited crystals only on violent shaking, and then in a dense cloud which was deposited on the glass and on the mica.

Some 40—50 observations were made at each of the initial temperatures 48·5° and 31·5°. The critical supercooling was 1·85° and 1·45°, and the standard deviation 0·24° and 0·13°, respectively. These degrees of supercooling correspond to a supersaturation ratio (concentration/solubility) of 1·008 and 1·007 at 46·65° and 30·05°, respectively (cf. Seidell, " Solubilities of inorganic and metal compounds," van Nostrand, 1940). In view of the small effect of temperature on the critical supercooling, readings at intermediate temperatures were not taken.

## Discussion

In order that a perfect crystal face may grow in a supersaturated solution a nucleus of the critical size must be formed. The number of molecules $n_c$ in the critical nucleus is given by

$$n_c^{\frac{1}{2}} = \eta g/(2kT \ln \alpha)$$

where $\eta$ is the edge energy per molecule, $g$ a packing factor such that the number of molecules in the edge of a nucleus containing $n_c$ molecules is $gn_c^{\frac{1}{2}}$, $k$ the Boltzmann constant, $T$ the absolute temperature, and $\alpha$ the supersaturation ratio (Frank, *loc. cit.*; Bradley, *Quart. Reviews*, 1951, **5**, 315). In these experiments, $\eta$ refers to the edge of an ammonium iodide crystal resting on mica and surrounded by solution. When mica is cleaved the potassium

ions probably divide equally between the two faces, forming a hexagonal arrangement of two-dimensional lattice points, half of which are occupied by potassium and half by negative holes. It seems likely that the nucleus of ammonium iodide could be formed on a suitable patch consisting largely of either potassium ions or negative holes, so that the nucleus is made up of a layer of cations and a layer of anions, one of which lies above the other.

The classical theory of surface nucleation gives for the rate of formation of nuclei in cm.$^2$ per sec. the value

$$I = C[\eta g/(8\pi kTn_c^{\frac{3}{2}})]^{\frac{1}{2}} \exp\,[-\Delta G_{max.}/(kT)]$$

where $C$ is a collision factor, and where

$$\Delta G_{max.} = \tfrac{1}{2}\eta g n_c^{\frac{1}{2}} = \tfrac{1}{2}\eta^2 g^2/(2kT \ln \alpha)$$

According to this result the rate of nucleation is highly dependent on temperature, since $\Delta G_{max.}$ is temperature-dependent. The result is that at a certain degree of supercooling a catastrophic nucleation sets in with an apparently sharp boundary, although theoretically nucleation will occur slowly at much smaller degrees of supercooling. It is usual to take $I = 1$ nucleus per cm$^2$. per sec. as the criterion for this catastrophe, slightly smaller or larger degrees of supercooling giving much smaller or greater rates, respectively.

It is usually considered in the light of the preceding two equations that surface nucleation would occur from the vapour on a perfect flat crystal surface at values of log $\alpha$ of the order of unity (Frank, *loc. cit.*; *Discuss. Faraday Soc.*, 1949, **5**, 48, 67). This is in contrast to Volmer and Schultze's experiments with iodine, since the experimental ln $\alpha$ is of the order 0·01 (*Z. physikal. Chem.*, 1931, *A*, **156**, 1), and the deviation is attributed to growth by a dislocation mechanism (Frank, *loc. cit.*). At first sight the results on ammonium iodide support the view that growth occurs on dislocation edges, since ln $\alpha \sim 0{\cdot}0075$. It seems unlikely, however, that the ammonium iodide could make use of the dislocation edges which are present on the surface, since the molecular step of the mica is much too large. Moreover, the orientation of the prisms of ammonium iodide suggests that the crystallisation is due to true surface nucleation; there are comparatively large patches of the mica which are molecularly plane. It seems more likely that, in contrast to the growth of crystals from the vapour, two-dimensional nucleation may occur from solution on a perfect crystal face at supersaturation ratios near to unity. We may attribute the low results for ammonium iodide to the small value of $\eta$, which would have to be approximately a tenth of the value for an iodine crystal growing from the vapour, a not unreasonable result. It seems possible, therefore, that these experiments refer to the unusual case of true two-dimensional nucleation on a perfect crystal face.

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## 873. *A Preliminary Study of the Main Polysaccharide of* Lupinus termis *Seeds.*

By Wadie Tadros and Mohamed Kamel.

*Lupinus termis* seeds are commonly used as edible material in Egypt. The same polysaccharide material was obtained on extraction of the powdered skinned seeds by (*a*) a method modified from that used for the extraction of the hemicellulose of the New Zealand flax (*Phormium tenax*) (McIlroy, Holmes, and Mauger, *J.*, 1945, 796), or (*b*) the procedure adopted by Hirst, Jones, and Walder (*J.*, 1947, 1225) for extraction of *Lupinus albus*. McIlroy *et al.* used 4% aqueous sodium hydroxide; in the present investigation, the same product was obtained with 0·5%, 1%, or 4% aqueous sodium hydroxide. The polysaccharide is built of D-galactose, L-arabinose, and a uronic acid, which since it affords mucic acid is D- or L-galacturonic acid.

Hirst *et al.* (*loc. cit.*) showed that associated with the galactan of *Lupinus albus* there was an araban which could be partly removed by extraction with 70% alcohol and a pectic acid which could be precipitated as calcium pectate. We failed to obtain an araban or pectic acid from our polysaccharide material.

In estimations of arabinose as its benzoylhydrazone (Hirst, Jones, and Woods, *J.*, 1947, 1048), it was found useful to add a weighed quantity of arabinose (about equal to that expected) which was then subtracted from the value obtained.

## Experimental

*Extraction.*—(*a*) After being soaked overnight in water the seeds (500 g.) were skinned and twice milled. The powder was extracted with water (2 l.) on a shaker for 4 hours and then filtered through muslin. This process was repeated three times. The cake thus obtained was extracted with 0·5% aqueous ammonium oxalate (2 l.) for 6 hours on a boiling-water bath to remove pectic substances (McIlroy *et al.*, *loc. cit.*). The residue, washed and pressed, was stirred with 4% aqueous sodium hydroxide for 12 hours at room temperature and heated on a boiling-water bath for 3 hours. The alkaline extract was filtered through muslin and the extraction was repeated (it was then complete). The combined filtrates were poured into alcohol (4 vols.), and the precipitated polysaccharide was purified by solution in water and reprecipitation by acidified alcohol. The polysaccharide material (A) was washed with alcohol, then ether, and dried in a vacuum at 100° over phosphoric oxide. It was a cream-coloured amorphous powder insoluble in cold water and sparingly soluble in hot water (yield, 10—15 g.) [Found (averages): total furfuraldehyde, 9·6; uronic anhydride, 8·4; araban, 14·3; methoxyl, 0; ash, 0; galactan by difference, 77·3%]. The same product was obtained on using 0·5% or 1% aqueous sodium hydroxide.

(*b*) After being soaked overnight in water, the seeds (500 g.) were stripped of their skins and milled twice. The protein matter was then extracted by stirring them with 10% aqueous sodium chloride for 3 hours, followed by filtration, and repetition of the process three times. The solid residue was then stirred with 0·2% aqueous sodium hydroxide thrice for 12 hours at a time. Addition of hydrochloric acid to the filtrate then gave no precipitate, indicating absence of appreciable quantities of protein. The solid residue was then boiled with 0·2% aqueous sodium hydroxide (2 l.) for 3 hours, after which it was filtered and the filtrate poured into alcohol (4 vols.). The precipitated polysaccharide was filtered off and redissolved in water. The aqueous solution was filtered and the polysaccharide (B) precipitated by addition of acidified alcohol, filtered off, washed until free from acid, and dried in a vacuum over phosphoric oxide at 100°. It was a cream-coloured powder (yield 12 g.) [Found (averages): total furfuraldehyde, 9·6; uronic anhydride, 8·4; araban, 14·3; methoxyl, 0; ash, 0; galactan by difference, 77·3%].

*Hydrolysis.*—The material A or B (4 g.) was boiled with 4% sulphuric acid (50 c.c.) for 5 hours until the reducing power (Bertrand method; Browne and Zerban, "Sugar Analyses," Chapman & Hall, London, 1948, p. 776) of the solution remained constant. The solution was neutralised with barium carbonate and filtered. The filtrate was concentrated under reduced pressure at 70°, and the syrupy product poured into alcohol (40 c.c.). The precipitated barium salt was filtered off and gave on oxidation with bromine (see below) mucic acid, m. p. 212° not depressed on admixture with an authentic sample. The filtrate was concentrated in vacuum at 70° to 10 c.c. Qualitative analysis showed the presence of arabinose (identified as its benzoylhydrazone, m. p. 190°, and as its diphenylhydrazone, m. p. 204°, both not depressed on admixture with authentic samples) and galactose (identified as its methylphenylhydrazone, m. p. 186° not depressed on admixture with an authentic sample). "Authentic" derivative were prepared from the above sugars.

Quantitative analysis of the hydrolysate (Hirst, Jones, and Woods, *loc. cit.*) gave 13·8% of arabinose and 79·4% of galactose.

*Oxidation* (cf. Heidelberger and Goebel, *J. Biol. Chem.*, 1927, **74**, 613).—A mixture of the material A or B (1·2 g.), 7·5% hydrobromic acid (12 c.c.), and bromine (0·6 c.c.) was heated on a boiling-water bath for 10 hours. A slight precipitate proved to be mucic acid, m. p. 212° alone or mixed with an authentic sample. On removal of mucic acid, no potassium hydrogen saccharate could be obtained from the filtrate, indicating the absence of glucuronic acid.

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Giza, Egypt. [*Received, July* 1*st*, 1952.]

## 874. 5-*Benziloyloxymethylfurfuryltrimethylammonium Chloride.*

By A. S. Bailey, D. H. Bates, and H. R. Ing.

The benzilic esters of choline and analogous alkamines have mydriatic properties (Ford-Moore and Ing, *J.*, 1947, 55) so that the discovery that 5-methylfurfuryltrimethylammonium iodide had intense acetylcholine-like activities (Ing, Kordik, and Tudor-Williams, *Brit. J. Pharmacol.*, 1952, **7**, 103) suggested that analogous compounds with a 5-benzilyloxymethyl group might be mydriatics. 5-Benziloyloxymethylfurfuryltrimethylammonium chloride was prepared but it had negligible activity when tested as a mydriatic in mice by Pulewka's method (see Ing, Dawes, and Wajda, *J. Pharmacol.*, 1945, **85**, 85); moreover, even large doses (2—4 mg.) did not prevent the vasodilator effect of 1 μg. of acetylcholine in the cat.

*Experimental.*—5-Hydroxymethylfurfuryldimethylamine was prepared as described by Ing, Kordik, and Tudor-Williams (*loc. cit.*), converted into its methiodide, m. p. 129°, and characterized as its *methopicrate*, which crystallized from ethanol, m. p. 125° (Found : C, 45·9; H, 4·9. $C_{15}H_{18}O_9N_4$ requires C, 45·2; H, 4·5%). The methochloride, prepared by means of silver chloride from the methiodide but not isolated, was covered with chloroform and treated with excess of thionyl chloride; after 24 hours at room temperature the reaction mixture was evaporated, finally *in vacuo*, and the 5-chloromethyl derivative characterized as its *picrate* which, crystallized from ethanol, had m. p. 116° (Found : C, 43·4; H, 4·0. $C_{15}H_{17}O_8N_4Cl$ requires C, 43·2; H, 4·1%). The crude methochloride (14·2 g.) was converted by heating with potassium benzilate (4·5 g.) in ethanol into the methobenzilate; removal of potassium chloride and evaporation of the solvent left a gum, which after being heated at 100° for 10 hours and subsequently treated with acetone gave solid 5-*benziloyloxymethylfurfuryltrimethylammonium chloride* (cf. Horenstein and Pahlicke, *Ber.*, 1938, **71**, 1654). The crude product, dissolved in ethanol, was passed through a charcoal column and recovered by evaporation of the solvent and treatment of the residue with acetone. The solid so obtained, purified by crystallization from hot acetone in which it was sparingly soluble, had m. p. 154° (decomp.) (Found : C, 65·6; H, 6·3. $C_{23}H_{26}O_4NCl$ requires C, 66·4; H, 6·2%).

5-Hydroxymethylfurfuryldiethylamine, prepared in the same way as the dimethylamino-compound, was converted into its *ethiodide* which, crystallized from ethanol–ethyl acetate, had m. p. 142° (decomp.) (Found : C, 42·7; H, 6·4. $C_{12}H_{22}O_2NI$ requires C, 42·5; H, 6·5%).

Department of Pharmacology, Oxford. [*Received, July 7th*, 1952.]

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## 875. 2-3′ : 5′-*Dihydroxyphenylethylamine and* 3 : 5-*Dihydroxyphenylalanine.*

By A. S. Bailey, D. H. Bates, H. R. Ing, and M. A. Warne.

3 : 5-Dihydroxyphenylalanine and its decarboxylation product, 2-3′ : 5′-dihydroxyphenylethylamine, were needed for studies on the substrate specificity of amino-acid decarboxylases (Blaschko, *Biochim. Biophys. Acta*, 1950, **4**, 130); the latter compound was also needed for pharmacological work on isomeric dihydroxyphenylethylamines.

*Experimental.*—Methylation of 3 : 5-dihydroxybenzoic acid (*Org. Synth.*, 1941, **21**, 27), followed by esterification (best through the acid chloride) and reduction by lithium aluminium hydride, gave 3 : 5-dimethoxybenzyl alcohol, which was readily converted by thionyl chloride and pyridine into 3 : 5-dimethoxybenzyl chloride, m. p. 43—45° (Adams, Mackenzie, and Loewe, *J. Amer. Chem. Soc.*, 1948, **70**, 664; Adams, Harfenist, and Loewe, *ibid.*, 1949, **71**, 1624).

The benzyl chloride (20 g.) in ethanol (50 ml.) was added slowly to a hot solution of potassium cyanide (20 g.) in water (20 ml.), and the mixture heated for 3 hours at 100°. The benzyl cyanide, isolated by extraction with ether, was obtained as a pale yellow solid (Adams, Mackenzie, and Loewe, *loc. cit.*, give m. p. 53°) (yield 85%). The cyanide (11 g.) in ether (100 ml.) was added to lithium aluminium hydride (4 g.) in ether (150 ml.) with stirring. After 1 hour the crude amine was isolated in the usual way and demethylated by slow distillation with

acetic acid (25 ml.), hydriodic acid (*d* 1·5; 25 ml.), and red phosphorus (2 g.). When methyl iodide ceased to distil, the solution was diluted, filtered, and evaporated *in vacuo*. The residue was crystallized repeatedly by slow evaporation of its aqueous solution *in vacuo* over phosphoric oxide, and 2-3′ : 5′-*dihydroxyphenylethylamine hydriodide* obtained as its monohydrate which began to decompose at 185° (Found: C, 32·3; H, 4·5; N, 4·6. $C_8H_{11}O_2N,HI,H_2O$ requires C, 32·1; H, 4·7; N, 4·7%).

3 : 5-Dimethoxybenzyl chloride (3·75 g.) was added to a solution of sodium (0·36 g.) and ethyl acetamidomalonate (3·4 g.) in ethanol. After being boiled for 2·5 hours, the solution was evaporated *in vacuo* and the solid residue treated with ice-water. The solid *ethyl acetamido-3 : 5-dimethoxybenzylmalonate* (6·8 g., 87%), recrystallized from light petroleum (b. p. 60—80°)–benzene, had m. p. 114° (Found: C, 59·9; H, 6·7. $C_{18}H_{27}O_7N$ requires C, 58·9; H, 6·8%). It (5 g.) was hydrolysed with concentrated hydrochloric acid–acetic acid (20 ml. of 1 : 1 by vol.); evaporation of the acid solution gave 3 : 5-*dimethoxyphenylalanine hydrochloride*, which crystallized from ethanol (Found: C, 50·7; H, 6·3. $C_{11}H_{10}O_4NCl$ requires C, 50·0; H, 6·1%). The amino-acid hydrochloride (1 g.) was demethylated by heating it with hydrobromic acid (*d* 1·5; 10 ml.) for 2·5 hours. Evaporation of the acid solution *in vacuo* left a brown residue; its aqueous solution was decolorized by passage through a charcoal column, concentrated, and treated with pyridine, which precipitated 3 : 5-*dihydroxyphenylalanine*. The amino-acid crystallized in prisms when its solution in hot water was cooled (Found: C, 54·5; H, 6·0. $C_9H_{11}O_4N$ requires C, 54·8; H, 5·6%).

DEPARTMENT OF PHARMACOLOGY, OXFORD. [*Received, July 7th*, 1952.]

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## 876. *Heat of Hydrolysis of Phosphorus Oxychloride and Phosphorus Trichloride.*

By E. NEALE and L. T. D. WILLIAMS.

As a preliminary to a study of the thermochemistry of alkyl halogenophosphinates and related compounds, the heats of hydrolysis of phosphorus oxychloride and phosphorus trichloride have been redetermined, a calorimeter of the Dewar-vessel type similar to that described by Bichowsky (*J. Amer. Chem. Soc.*, 1923, **45**, 2225) being used. The reactions are:

$$POCl_3 + x_1H_2O \longrightarrow H_3PO_4 \text{ aq.} + 3HCl \text{ aq.}$$

and

$$PCl_3 + x_2H_2O \longrightarrow H_3PO_3 \text{ aq.} + 3HCl \text{ aq.}$$

where $x_1$ and $x_2$ varied from 2600 to 4300 and 4500 to 7500 respectively. Heats of formation were calculated from the results by using values for $Q_f(H_2O \text{ liq.})$, $Q_f(HCl \text{ aq.})$, $Q_f(H_3PO_4 \text{ aq.})$, and $Q_f(H_3PO_3 \text{ aq.})$ given in "Selected Values of Chemical Thermodynamic Properties" (Nat. Bur. Standards, Washington, 1947). The mean results are given below together with the existing published values taken from Bichowsky and Rossini's "Thermochemistry of Chemical Substances," Reinhold Publ. Corpn., N.Y., 1936 (B. and R.), and the "Selected Values, etc." (N.B.S.). Both sets of published values for heat of formation are derived from J. Thomsen's results on heats of hydrolysis ("Thermochemische Untersuchungen," S. A. Barth, Leipzig, 1882, Vol. II), but the Nat. Bur. Standards' publication uses revised values for heat of formation and solution of the products of hydrolysis.

| | New value (kcal. mole$^{-1}$) | B. & R. 1936 (kcal. mole$^{-1}$) | N.B.S. 1947 (kcal. mole$^{-1}$) |
|---|---|---|---|
| $POCl_3$ $Q$aq. | 79·9 ± 0·3 | 72·2 | — |
| $Q_f$(L) | 144·4 | 147·1 | 151·0 |
| $PCl_3$ $Q$aq. | 67·5 ± 0·3 | 65·1 | — |
| $Q_f$(L) | 79·6 | 76·9 | 81·0 |

Similar measurements on alkyl-substituted derivatives will be reported later.

The accuracy of our results was not high. Since the materials are sensitive to moisture, it is likely that in earlier work, precautions were inadequate. We used the dry-box technique in handling these materials.

The heat of hydrolysis of phosphorus oxychloride has also been measured independently at Manchester University (Dr. Skinner, personal communication) where results were similar to ours though slightly higher.

Acknowledgments are made to the Chief Scientist, Ministry of Supply, for permission to publish these results.

CHEMICAL DEFENCE EXPERIMENTAL ESTABLISHMENT,
PORTON, NEAR SALISBURY, WILTS.

[*Received, July 14th*, 1952.]

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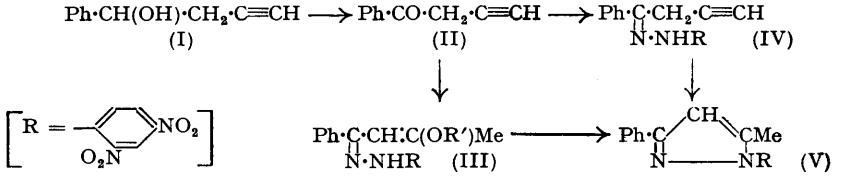
## 877. *Phenyl Propargyl Ketone.*

By H. B. HENBEST.

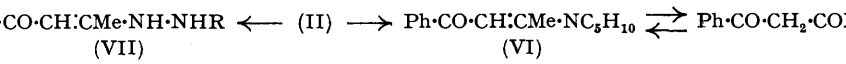
THE modified Reformatsky reaction between benzaldehyde and propargyl bromide in the presence of zinc yields the alcohol (I) (Henbest, Jones, and Walls, *J.*, 1949, 2696). Oxidation of (I) by means of the chromic acid–acetone technique of Bowden, Heilbron, Jones, and Weedon (*J.*, 1946, 39) has been found to give (crystalline) phenyl propargyl ketone (II) in 50% yield, thus providing a convenient route to a member of the little investigated class of β-keto-acetylenic compounds.

Treatment of the ketone with methanolic 2 : 4-dinitrophenylhydrazine sulphate solution afforded a red derivative, shown by analysis to contain a methoxy-group. Since this compound showed maximal light absorption at an appreciably longer wave-length (3910 Å) than acetophenone 2 : 4-dinitrophenylhydrazone (3780 Å), it was evident that it corresponds to structure (III; R′ = Me), the methoxyl group probably contributing to the bathochromic shift as it is attached terminally to the conjugated system (see, *inter al.*, Bowden, Braude, and Jones, *J.*, 1946, 948). With an ethanolic reagent the corresponding ethoxy-derivative (III; R′ = Et) was formed. The (orange) propargyl ketone 2 : 4-




dinitrophenylhydrazone (IV) could be obtained when 95% ethanol or, better, aqueous dioxan was used for the reagent solution. The derivative (IV) gave an insoluble silver salt, and displayed light-absorption properties similar to those of acetophenone 2 : 4-dinitrophenylhydrazone. The compounds (III; R′ = Me or Et) and (IV) were converted into a yellow product when warmed in methanol containing 10% of sulphuric acid. Compared with the 2 : 4-dinitrophenylhydrazones, this was more basic, exhibited no high intensity absorption in the 3700—3900-Å region, and showed no NH stretching frequency in the infrared spectrum; it is therefore formulated as the pyrazole (V).

Amines such as piperidine do not add rapidly to acetylenic linkages unless there is an adjacent electron-attracting group (cf. addition of amines to α-keto-acetylenes; Bowden, Braude, Jones, and Weedon, *J.*, 1946, 45). However, phenyl propargyl ketone reacted




very rapidly with piperidine to give the piperidino-ketone (VI), previously obtained by Cromwell and Witt (*J. Amer. Chem. Soc.*, 1943, **65**, 308) by heating benzoylacetone with piperidine—as found by these authors, the amine-adduct is very easily hydrolysed to benzoylacetone by dilute acid. It is likely that the relatively ready addition of piperidine to this β-keto-acetylene is due to an initial prototropic change induced by the amine,

forming the isomeric allene-ketone, which would then add piperidine very readily, thus leading to (VI). [A similar mechanism probably operates in the addition of alcohols to give the derivatives (III).] Inductive activation of the triple bond by the keto-group (*via* the methylene group) can be ruled out, because addition of piperidine would then take place in the reverse direction to that observed. Addition of the weaker base, 2 : 4-dinitrophenylhydrazine [to give (VII)], occurred if a small amount of 1-ethylpiperidine was used to effect the initial prototropic change.

## Experimental

M.p.s were taken on a Kofler block and are corrected; infra-red spectra were determined with a Perkin–Elmer double beam spectrometer by Dr. G. D. Meakins of this Department.

*Phenyl Propargyl Ketone* (*1-Phenylbut-3-yn-1-one*) (II) *and its Derivatives.*—To 1-phenylbut-3-yn-1-ol (14·5 g.) in acetone (70 c.c.) at 5°, chromic acid (7 g.) in sulphuric acid (6 c.c.) and water (20 c.c.) was added dropwise with stirring, the internal temperature being kept at 5°. The mixture was then stirred at 20° for 10 minutes, and the ketone isolated with ether. The crude solid product was triturated with methanol–water (3 : 2), to give almost pure ketone (7·5 g.), m. p. 75—83°. Recrystallization from light petroleum (b. p. 60—80°) gave *phenyl propargyl ketone*, m. p. 78—82° (Found: C, 83·0; H, 5·4. $C_{10}H_8O$ requires C, 83·3; H, 5·6%). Light absorption in ethanol: Max., 2450 Å; $\varepsilon = 12{,}700$ (for acetophenone, Ley and Wingchen, *Ber.*, 1934, **67**, 501, give max., 2400 Å; $\varepsilon = 13{,}200$). Infra-red absorption (on the supercooled melted solid): 3290 (medium strength; $C{\equiv}C{\overset{\longleftrightarrow}{-}}H$ stretching frequency) and 1690 cm.$^{-1}$ (strong; $C{\overset{\longleftrightarrow}{=}}O$ stretching frequency). Addition of ammoniacal silver nitrate solution to an alcoholic solution of the ketone precipitated a pale yellow silver derivative, further confirming the presence of a terminal ethynyl group. The ketone was unstable towards alkali (*e.g.*, soft glass), and was best kept in a Pyrex tube at 0°.

The ketone (0·3 g.) in methanol (5 c.c.) was added to 2 : 4-dinitrophenylhydrazine reagent [20 c.c. of a solution prepared by dissolving the base (2 g.) in sulphuric acid (7 c.c.) and methanol (100 c.c.)] at 20°. After a minute an orange solid began to separate and the mixture was then kept at 0° for 1 hour. Water and benzene were added, and the benzene solution was chromatographed on alumina (P. Spence, Grade H). The main band was eluted with benzene, and the product recrystallized from ethyl acetate–methanol (1 : 1), to give *3-methoxy-1-phenylbut-2-en-1-one* 2 : 4-*dinitrophenylhydrazone* (III; R′ = Me) as orange-red needles (changing to vermilion prisms when left overnight in contact with the mother liquor), m. p. 175—176° (Found: C, 57·4; H, 4·5; OMe, 8·5. $C_{17}H_{16}O_5N_4$ requires C, 57·3; H, 4·55; OMe, 8·7%). Light absorption (in chloroform): Max., 3910 Å; $\varepsilon = 26{,}500$; Min., 3220 Å; $\varepsilon = 3800$. Infra-red spectrum (in Nujol): NH stretching frequency at 3275 cm.$^{-1}$.

Substitution of ethanol for methanol in the preparation of the 2 : 4-dinitrophenylhydrazone gave the corresponding *ethoxy*-derivative (III; R′ = Et) crystallizing from dioxan–ethanol (1 : 1) as vermilion leaflets, m. p. 166—168° (Found: C, 58·5; H, 4·9. $C_{18}H_{18}O_5N_4$ requires C, 58·35; H, 4·9%). Light absorption (in chloroform): Max., 3910 Å; $\varepsilon = 28{,}400$; Min., 3220 Å; $\varepsilon = 3600$.

A solution of the propargyl ketone (0·2 g.) in dioxan (10 c.c.) was added to 2 : 4-dinitrophenylhydrazine (0·3 g.) dissolved in 2N-hydrochloric acid (100 c.c.). A flocculent yellow precipitate formed quickly; after 15 minutes sufficient benzene was added to dissolve the separated solid. The benzene layer was evaporated under reduced pressure to *ca.* 30 c.c., most of the propargyl derivative being precipitated. Recrystallization from ethyl acetate afforded *phenyl propargyl ketone* 2 : 4-*dinitrophenylhydrazone* (IV) as small orange needles, m. p. 193—195° (Found: C, 59·1; H, 3·65. $C_{16}H_{12}O_4N_4$ requires C, 59·25; H, 3·75%). Light absorption (in chloroform): Max., 3760 Å; $\varepsilon = 27{,}200$; Min., 3120 Å; $\varepsilon = 3600$ (cf. light absorption of acetophenone 2 : 4-dinitrophenylhydrazone in chloroform: Max., 3780 Å; $\varepsilon = 28{,}000$; Min., 3140 Å; $\varepsilon = 3500$). Infra-red spectrum (in Nujol): NH stretching frequency at 3280 cm.$^{-1}$. An orange gelatinous precipitate formed immediately when a solution of silver nitrate in methanol was added to a solution of the derivative in dioxan, confirming the presence of a terminal ethynyl group (2 : 4-dinitrophenylhydrazones not containing such a group do not give a precipitate).

A solution of each of the foregoing derivatives (50 mg.) in methanol (4 c.c. containing 10% of sulphuric acid) was heated under reflux for 1 minute. In each case, the solution became very pale yellow. Benzene and aqueous potassium hydrogen carbonate solution were added and the

product was purified by chromatography. Recrystallization from ethanol afforded in each case a good yield of 1-(2 : 4-*dinitrophenyl*)-5-*methyl*-3-*phenylpyrazole* (V) as lemon-yellow plates, m. p. 153—154° (Found : C, 59·25; H, 4·0. $C_{16}H_{12}O_4N_4$ requires C, 59·25; H, 3·75%). Light absorption (in ethanol) : Max., 2460 and 3350—3500 Å; $\varepsilon$ = 24,400 and 8100; Min., 2880 Å; $\varepsilon$ = 6000. Infra-red spectrum (in Nujol) : NH stretching band at *ca.* 3300 cm.$^{-1}$ absent.

*Addition of Piperidine to* (II).—Addition of piperidine (250 mg.) to the ketone (250 mg.) in dry ether (6 c.c.) occurred exothermally, and after 5 minutes the solvent was removed under reduced pressure, to give a solid product. Recrystallization from light petroleum (b. p. 60—80°)–benzene (4 : 1) gave the adduct (VI) (320 mg.) as prisms, m. p. 99°, undepressed on admixture with a sample prepared by Cromwell and Witt's method (*loc. cit.*). Light absorption : Max., 2480 and 3400 Å; $\varepsilon$ = 10,500 and 26,500 respectively. Bowden, Braude, and Jones (*J.*, 1946, 948) give for the light absorption of the related compound, Ph·CO·CH:CH·NEt$_2$, Max., 2430 and 3430 Å ($\varepsilon$ = 12,000 and 26,000 respectively).

*Addition of* 2 : 4-*Dinitrophenylhydrazine to* (II).—1-Ethylpiperidine (1 drop) was added to a solution of phenyl propargyl ketone (0·3 g.) and 2 : 4-dinitrophenylhydrazine (0·35 g.) in dry dioxan (20 c.c.). After 2 days at 20° about half of the solvent was removed under reduced pressure, water (2 c.c.) was added, and the mixture kept at 0° overnight. The solid which had separated was crystallized from ethyl acetate–methanol (1 : 1), to yield 3-(2 : 4-*dinitrophenylhydrazino*)-1-*phenylbut*-2-*en*-1-*one* (VII) (0·28 g.) as flat red needles, m. p. 157—158° (a second crystalline form was obtained from the mother-liquors as orange-red plates, showing identical m. p. and light absorption characteristics) (Found : C, 56·05; H, 4·25. $C_{16}H_{14}O_5N_4$ requires C, 56·15; H, 4·1%). Light absorption in chloroform : Max., 3620 Å; $\varepsilon$ = 21,600; Min., 2980 Å; $\varepsilon$ = 3000. Infra-red spectrum (in Nujol) : NH stretching at 3340 cm.$^{-1}$; C=O stretching at 1685 cm.$^{-1}$ (no absorption bands were shown in the 1650—1750 cm.$^{-1}$ region by the 2 : 4-dinitrophenylhydrazones described above).

THE UNIVERSITY, MANCHESTER, 13. [*Received, July 16th*, 1952.]

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## 878. *The Preparation of Silver Tetrafluoroborate and Silver(I) Fluoride.*

By A. G. SHARPE.

PREVIOUS attempts to make anhydrous silver fluoroborate have all failed (see Booth and Martin, "Boron Trifluoride and its Derivatives," John Wiley and Sons, 1949; Warf, Abstr., XIIth Meeting, Int. Congr. Pure and Applied Chem., New York, 1951). Woolf and Emeléus (*J.*, 1950, 1050) showed that bromine trifluoride converts borax into sodium tetrafluoroborate, and by the action of this reagent on silver borate silver tetrafluoroborate has now been prepared.

Silver fluoroborate is strikingly similar to silver perchlorate, the remarkable properties of which are summarised by Sidgwick ("The Chemical Elements and their Compounds," Oxford Univ. Press, 1950). It is deliquescent, very soluble in water, ether, and toluene, moderately soluble in benzene and *cyclo*hexene, and insoluble in *cyclo*hexane; these observations indicate $\pi$-bond formation between the aromatic or unsaturated compounds and the silver ion, similar to that found in the silver perchlorate–benzene complex by Rundle and Goring (*J. Amer. Chem. Soc.*, 1950, **72**, 5337). With iodine, silver fluoroborate forms a powerful iodinating mixture analogous to iodine and silver perchlorate (Birckenbach and Goubeau, *Ber.*, 1932, **65**, 395; Haszeldine and Sharpe, *J.*, 1952, 993). The stoicheiometry of the very fast reaction between iodine, silver fluoroborate, and phenol indicates that it proceeds according to the equation $C_6H_5{\cdot}OH + I_2 + AgBF_4 = C_6H_4I{\cdot}OH + AgI + HF + BF_3$. Toluene and ether are also attacked by the mixture at room temperature; the relative rates of attack (measured by the loss in oxidising power of the solution) show that iodine and silver fluoroborate form an iodinating mixture about as powerful as iodine and silver perchlorate, and considerably more powerful than iodine and silver trifluoroacetate (Haszeldine and Sharpe, *loc. cit.*).

Thermal decomposition of silver fluoroborate into argentous fluoride and boron

trifluoride takes place rapidly at 200°. Treatment of silver borate with liquid bromine trifluoride, followed by heating of the product at this temperature, therefore affords a rapid method for the preparation of small quantities of dry argentous fluoride for use in halogen-exchange reactions; the entire preparation may be carried out in quartz apparatus.

EXPERIMENTAL

Dry silver borate, prepared from silver nitrate and boric acid, was treated with bromine trifluoride as described by Sharpe and Emeléus (*J.*, 1948, 2135). The white residue of *silver tetrafluoroborate*, insoluble in bromine trifluoride, gave only a trace of silver bromide (derived from silver tetrafluorobromite, $AgBrF_4$, present as an impurity) on addition of water. Soluble silver was determined as chloride, and $BF_4^-$ as the nitron salt (Lange, *Ber.*, 1926, **59**, 210) (Found: Ag, 54·5; $BF_4$, 44·0. $AgBF_4$ requires Ag, 55·3; $BF_4$, 44·7%). The salt decomposed without melting at 200° when heated in a flask attached to a vacuum line, giving an orange residue of argentous fluoride containing only a little silver bromide (Found: Ag, 83·0. Calc. for AgF: Ag, 85·3%). An *X*-ray powder photograph of the residue showed it to have a face-centred cubic lattice with $a = 4{\cdot}94$ Å; Ott (*Z. Krist.*, 1926, **63**, 222) found $a = 4{\cdot}92$ Å for a sample made from the oxide and hydrofluoric acid. Decomposition of silver tetrafluorobromite under identical conditions does not yield a homogeneous product; some silver difluoride appears to be formed, and there is marked attack on the reaction vessel.

Iodine (0·182 g., 0·72 m-mole) and phenol (0·072 g., 0·75 m-mole) in "AnalaR" benzene were added to silver fluoroborate (0·139 g., 0·72 m-mole) in the same solvent, which is iodinated much less readily than phenol. The colour of iodine at once disappeared, and a gas which fumed strongly in moist air was liberated. The solution was immediately filtered on a Gooch crucible; the filtrate did not liberate iodine from aqueous potassium iodide; the precipitated silver iodide weighed 0·159 g. (0·68 m-mole).

A solution of silver fluoroborate (0·154 g., 0·79 m-mole) and phenol (2 g., excess) in toluene was titrated with a standard solution of iodine in toluene until the colour of iodine appeared in the solution; this end-point corresponded to addition of 0·190 g. (0·75 m-mole) of iodine. The solution was at once filtered, and silver iodide (0·186 g., 0·79 m-mole) equivalent to all of the silver and to one-half of the iodine taken was obtained. These results are similar to those previously obtained with silver perchlorate and silver trifluoroacetate.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, July 16th*, 1952.]

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## 879. *The Action of Methylmagnesium Iodide on Two Nitramines.*

By ALEX. H. LAMBERTON.

ONE mol. of gas was immediately evolved when ethereal methylmagnesium iodide was added to an equimolar quantity of methylnitramine in ether. An attempt to alkylate the crude reaction product failed: some methylnitramine was recovered. No gas was evolved in a reaction with nitromorpholine; instead, a solid addition compound (1 : 1) was precipitated in excellent yield. Reduction of this complex with zinc and hydrochloric (or acetic) acid, followed by distillation from an alkaline medium, yielded mixed volatile bases, of which only morpholine was identified. In general it appeared that methylnitramine reacted simply as an acid, whilst the secondary nitramine behaved in a manner more appropriate to *C*-nitro-compounds (Buckley, *J.*, 1947, 1492). No evidence, however, was obtained of the formation of methylmorpholinylhydrazine by reduction of the addition complex.

*Experimental.*—Ethereal methylmagnesium iodide (20 ml.; containing 17 ± 1 mmoles, determined according to Gilman *et al.*, *J. Amer. Chem. Soc.*, 1923, **45**, 153) was added, in a closed system, dropwise in 15 minutes at 17° to a stirred solution of methylnitramine (16·9 mmoles in 30 ml. of ether), giving a semi-solid precipitate. The gas (17·2 ± 0·5 mmoles), evolved concurrently with the addition, passed through a sulphuric acid bubbler and was measured by displacement of water.

Addition of methyl iodide (17 mmoles in 10 ml. of ether) and subsequent refluxing for 2 hours produced no apparent change in the precipitate. Next morning the salt was decomposed by 2N-hydrochloric acid (20 ml.). No neutral material was obtained on working up, but crude methylnitramine (6·7 mmoles; coloured, but of m. p. 35—37°, undepressed by mixture with authentic material) was recovered from a sodium hydroxide extract of the ethereal layer.

Ethereal methylmagnesium iodide (20 ml.; containing 22·5 mmoles) was added similarly in 25 minutes to 4-nitromorpholine (22·7 mmoles in 40 ml. of ether). Less than 1 mmole gas was evolved. The 1 : 1 addition *complex* precipitated (6·11 g., 90%) was collected, washed with ether, and dried *in vacuo* (Found: C, 19·6; H, 4·5; Mg, 8·0. $C_4H_8O_3N_2,CH_3MgI$ requires C, 20·1; H, 3·7; Mg, 8·1%). On storage *in vacuo* the main bulk of this hygroscopic material remained colourless, but the surface exposed to light became yellow.

The addition complex (10 mmoles) was heated on the water-bath for 2 hours with granulated zinc (7·5 g.) and 5N-hydrochloric acid (60 ml.). After basification with sodium hydroxide the volatile bases liberated (9·3 milliequivs.) were steam-distilled into standard hydrochloric acid. Evaporation of the distillate yielded a mixture of hydrochlorides (Equiv., by weight of solid per equiv. of base, 104; by determination of Cl′, 98), and attempts to isolate a pure salt by crystallisation were unsuccessful. By the Schotten–Baumann reaction the crude material gave 4-toluene-*p*-sulphonylmorpholine (*ca.* 35% on the morpholine content of the complex), m. p. 146—147°, undepressed by mixture with an authentic sample. In another experiment a small quantity of alcohol-insoluble material (m. p. >250°; equiv., 55; apparently ammonium chloride) was isolated.

The addition complex (6·3 mmoles) was added to ice-water (20 ml.) and zinc dust (10 g.). Acetic acid (10 ml. of 50%) was added portionwise, with shaking and cooling in ice. After 1½ hours the mixture was warmed on the water-bath for 25 minutes, basified, and steam-distilled. The distillate contained 3·3 milliequivs. of base, and the crude hydrochlorides obtained on evaporation yielded 4-toluene-*p*-sulphonylmorpholine (14% on morpholine content of complex).

THE UNIVERSITY, SHEFFIELD, 10. [*Received, July 19th*, 1952.]

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## 880. *An Improved Synthesis of Pyridine-2-aldehyde.*

By E. P. HART.

PYRIDINE-2-ALDEHYDE has been prepared in moderate or poor yield by several methods (see Dyson and Hammick, *J.*, 1939, 781; Kaufmann and Vallette, *Ber.*, 1912, **45**, 1736; 1913, **46**, 49; Niemann *et al.*, *J. Amer. Chem. Soc.*, 1942, **64**, 1678). Although Harries and Lénárt's method (*Annalen*, 1915, **410**, 95) also gives a poor yield of impure product, we have modified it so as to obtain the aldehyde in better yield and quality.

*Experimental.*—A slow stream (5 c.c./min.) of ozonised oxygen (10% of ozone) was passed during 1 hour into 2-stilbazole (Harries and Lénárt, *loc. cit.*) (5 g.) in dry ethyl acetate (100 c.c.), cooled to between −15° and −20°. Decomposition of the ozonide was accomplished by addition of water (10 c.c.), zinc dust (0·5 g.), N/10-silver nitrate (1 c.c.), and quinol (0·05 g.). After being kept overnight, the mixture was extracted with 3·7% hydrochloric acid (2 × 20 c.c.), and the extract heated on the water-bath to complete removal of benzaldehyde. The pyridine-2-aldehyde, b. p. 69—70°/16 mm. (1·7 g., 57%), was isolated after addition of aqueous potassium hydroxide and extraction with ether. Its yield is diminished if the quantities used are more than double those given.

The author is indebted to Dr. E. Tittensor for his interest in this work.

THE TECHNICAL COLLEGE, NOTTINGHAM. [*Received, July 23rd*, 1952.]

## 881. *The Preparation of Arylalkanesulphonic Acids.*

By C. A. Bunton and E. A. Halevi.

In the course of a kinetic investigation it was necessary to prepare the sodium salts of a number of arylalkanesulphonic acids. The accepted method of preparation by heating the appropriate arylalkyl halide with aqueous sodium sulphite (see, *e.g.*, Suter, "Organic Chemistry of Sulphur," Wiley, N.Y., 1944, p. 114) was satisfactory with the bromides but not with the corresponding chlorides. As the chlorides can usually be prepared easily by chloromethylation, the general method was modified so as to utilize the chloride. This is converted into the corresponding iodide by treatment with sodium iodide in acetone solution; the iodide, which need not be isolated, is then converted into the sulphonate, in good yield, by warming it with sodium sulphite in aqueous acetone.

The simplicity and rapidity of this procedure, as well as its apparent generality, prompt us to report it.

*Experimental.*—The preparation of two typical sulphonates is described, one with, and the other without, prior isolation of the intermediate iodide.

Repeated microanalyses of these sodium sulphonates, as well as others prepared by the older method, yielded unsatisfactory and inconsistent results for carbon and hydrogen. They were therefore characterised as the *S*-benzylthiuronium derivatives (Chambers and Watt, *J. Org. Chem.*, 1941, **6**, 376).

(I) (a) *5-Methoxy-2-methylbenzyl iodide.* A solution of 2-methoxy-5-methylbenzyl chloride (17 g., 0·10 mole) (Ducasse, *Bull. Soc. chim.*, 1935, **2**, 1283; Quelet, *Compt. rend.*, 1934, **198**, 102) and sodium iodide (16·5 g., 0·11 mole) in acetone (100 c.c.) is warmed gently on a steam-bath for 15 minutes, and allowed to cool. The mixture is filtered, and the retained sodium chloride washed with a further 50 c.c. of acetone. The combined acetone solutions are poured on ice, and the *5-methoxy-2-methylbenzyl iodide* purified by recrystallisation from light petroleum as a pale yellow crystalline powder, m. p. 45—46°, decomp. on storage. An air-dried, freshly prepared sample was analysed (Found: I′, 47·9, 48·0. $C_9H_{11}OI$ requires I′, 48·4%).

(b) *Sodium 5-methoxy-2-methyltoluene-ω-sulphonate.*—The bulk of the uncrystallised iodide is redissolved in acetone (100 c.c.), and a solution of 27·5 g. (0·11 mole) of sodium sulphite ($Na_2SO_3,7H_2O$) in 100 c.c. of water added. The mixture is refluxed for 15 minutes, and the acetone boiled off. The hot aqueous solution is filtered, and the product allowed to crystallise slowly. The crystals are collected, and washed once with 10 c.c. of cold water and several times with alcohol. The *sodium* salt was further recrystallised from water and dried at 110° (Found: Na, 9·7. $C_9H_{11}O_4SNa$ requires Na, 9·7%). The S-*benzylthiuronium* derivative melted at 164° (Found: C, 53·6; H, 6·3; N, 7·4. $C_{17}H_{22}O_4N_2S_2$ requires C, 53·4; H, 6·0; N, 7·3%).

(II) *Sodium* iso*durene-α²-sulphonate* (*mesitylmethanesulphonate*). α²-Chloro*iso*durene (17 g., 0·10 mole) (*Org. Synth.*, 1945, **25**, 65) is treated with sodium iodide in acetone as in (I) (a). The iodide is not isolated but, after removal of the sodium chloride by filtration, is converted directly into *sodium mesitylmethanesulphonate* by warm aqueous sodium sulphite as in (I) (b) (Found: Na, 9·9. $C_{10}H_{13}O_3SNa$ requires Na, 9·7%). The *benzylthiuronium* derivative melted at 151° (Found: C, 55·3; H, 6·1; N, 7·4. $C_{18}H_{24}O_3N_2S_2$ requires C, 55·7; H, 6·1; N, 7·6%).

The yield is approximately 60%, based on the arylalkyl chloride. No attempt was made to improve the yield by working up the mother-liquors.

The authors are indebted to Professor E. D. Hughes, F.R.S., for his interest, and to the Humanitarian Trust and the Friends of the Hebrew University of Jerusalem for a maintenance grant to one of them (E. A. H.).

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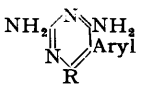
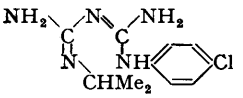
## 882. 3 : 5-*Diamino*-1-*aryl*-1 : 2 : 4-*triazoles as Potential Antimalarials.*

By (Miss) J. P. Thurston and James Walker.

The discovery of outstanding antimalarial activity in 2 : 4-diamino-5-arylpyrimidines (I; R = H or alkyl) (Falco, Goodwin, Hitchings, Rollo, and Russell, *Brit. J. Pharmacol.*, 1951, **6**, 185; Chase, Thurston, and Walker, *J.*, 1951, 3439) and the announcement that the active metabolite of proguanil (II) is 4 : 6-diamino-1-*p*-chlorophenyl-1 : 2-dihydro-2 : 2-dimethyl-1 : 3 : 5-triazine (III) (Carrington, Crowther, Davey, Levi, and Rose, *Nature*, 1951, **168**, 1080) suggested that noteworthy antimalarial activity might be found in other series of compounds containing the same common fragment $-N{:}C(NH_2){\cdot}N{:}C(NH_2){\cdot}X(Aryl)-$ (IV; X = C or N), an expectation which is borne out in the *as*-triazine series (V) (cf. Hitchings, Maggiolo, Russell, VanderWerff, and Rollo, *J. Amer. Chem. Soc.*, 1952, **74**, 3201).

We have examined a series of 3 : 5-diamino-1-aryl-1 : 2 : 4-triazoles (1-arylguanazoles) (VI), in which the six-membered hetero-ring of (I) and (III) has been replaced by a five-membered ring and in which the apparently significant grouping (IV; X = N) is included. None of these (VI; R = Ph, *p*-chlorophenyl, 2 : 4-dichlorophenyl, or 3 : 4-dichlorophenyl) showed detectable activity against *Plasmodium berghei* in the mouse at dosage levels


(I)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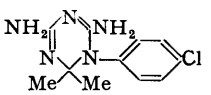
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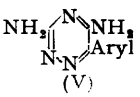
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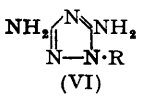
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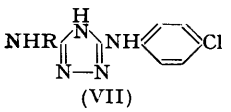
(VII)

greatly in excess of the levels at which (I), (II), and (III) are fully active; (VI; R = *p*-chlorophenyl) was also inactive against *P. gallinaceum* in the chick. The compounds (VI) were prepared by reaction between the appropriate arylhydrazines and dicyandiamide following generally Cohn's method (*J. pr. Chem.*, 1911, **84**, 409). As far as we are aware, the only other substance of this type which has been examined is (VI; R = *p*-bromophenyl), which has recently been found to be inactive (Hitchings *et al.*, *loc. cit.*), while the related series of 3-alkylamino-5-*p*-chloroanilino-1 : 2 : 4-triazoles (VII) also appears to be devoid of antimalarial activity (Curd, Davey, Richardson, and Ashworth, *J.*, 1949, 1739).

### Experimental

3 : 5-*Diamino*-1-*phenyl*-1 : 2 : 4-*triazole* (VI; R = Ph).—A mixture of phenylhydrazine hydrochloride (14·4 g.), dicyandiamide (8·4 g.), and water (30 c.c.) was boiled under reflux for 2 hours, then cooled, treated with charcoal, and basified with a slight excess of 2N-sodium hydroxide, whereupon the pure product separated in colourless needles (11·4 g., 65%). It was recrystallised from ethanol and had m. p. 174—175°, as recorded by Pellizzari (*Gazzetta*, 1891, **21**, ii, 146).

The following 3 : 5-*diamino*-1-*aryl*-1 : 2 : 4-*triazoles*, all of which separated from alcohol in prisms, were prepared in an analogous manner from the appropriate arylhydrazines: 1-*p*-*chlorophenyl*- (yield 93%), m. p. 198—199° (Found: C, 45·4; H, 4·1; N, 33·5. $C_8H_8N_5Cl$ requires C, 45·7; H, 3·8; N, 33·4%); 1-(2 : 4-*dichlorophenyl*)- (yield 75%), m. p. 182—184° (Found: C, 39·1; H, 2·9; N, 28·2. $C_8H_7N_5Cl_2$ requires C, 39·3; H, 2·9; N, 28·7%); 1-(3 : 4-*dichlorophenyl*)- (yield 95%), m. p. 204—205° (Found: C, 39·0; H, 3·1; N, 28·7%).

Biological tests were carried out in the manner previously described (Chase, Thurston, and Walker, *loc. cit.*).

The authors are indebted to Miss M. M. Cameron and Mr. R. J. Clark for technical assistance.

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The Ridgeway, Mill Hill, London, N.W.7.

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## 883. *The Vapour Pressure of Aqueous Solutions of Beryllium Sulphate and of Uranyl Sulphate at 25°.*

By R. A. Robinson.

The osmotic and activity coefficients of three uranyl salts have been measured recently (Robinson and Lim, *J.*, 1951, 1840). Measurements have also been made on uranyl sulphate (Secoy, *J. Amer. Chem. Soc.*, 1948, **70**, 3450) which indicate that this sulphate is anomalous at more than 1 *m*-concentrations, its activity coefficient being considerably higher than that of magnesium, zinc, or cadmium sulphate. This conclusion is derived from freezing-point measurements which yield activity coefficients at temperatures which decrease as the concentration increases. Thus an activity coefficient of 0·274 for uranyl sulphate at 3·5*m* and about −30° is compared with a value of 0·048 for zinc sulphate at the same concentration but at 25°. The heat-content and heat-capacity data necessary to correct over this temperature range are not available and Secoy could, therefore, do no more than draw attention to this anomaly. It is possible, however, that the anomaly results from a comparison of activity coefficients at very different temperatures rather than any peculiarity in the behaviour of uranyl sulphate. I have, therefore, measured vapour pressures of aqueous solution of this salt at 25° for direct comparison with those of other bivalent sulphates.

"AnalaR" beryllium sulphate has become available and the vapour pressures of solutions of this salt have been measured for comparison with those of magnesium sulphate (Robinson and Jones, *ibid.*, 1936, **58**, 959).

"AnalaR" $BeSO_4,4H_2O$ was used without further purification (Found : $SO_4$, 54·14. Calc. 54·23%). Uranyl sulphate was prepared by addition of a slight excess of uranium trioxide to sulphuric acid, analysis of the solution for both U and $SO_4$, and addition of the amount of sulphuric acid required to give the exact stoicheiometric ratio. The ratio was checked by a further analysis. Isopiestic vapour-pressure measurements were made, sodium chloride being used as reference salt, with the results given in Table 1. A comparatively large number

Table 1. *Molalities of isopiestic solutions of sodium chloride and beryllium sulphate or uranyl sulphate at 25°.*

| $BeSO_4$ | NaCl | $BeSO_4$ | NaCl | $BeSO_4$ | NaCl | $BeSO_4$ | NaCl | $BeSO_4$ | NaCl |
|---|---|---|---|---|---|---|---|---|---|
| 0·1022 | 0·06323 | 0·5671 | 0·3298 | 1·128 | 0·7268 | 2·205 | 1·824 | 3·135 | 3·147 |
| 0·1224 | 0·07510 | 0·5760 | 0·3362 | 1·272 | 0·8458 | 2·457 | 2·146 | 3·229 | 3·298 |
| 0·1304 | 0·8004 | 0·6621 | 0·3922 | 1·280 | 0·8531 | 2·497 | 2·206 | 3·429 | 3·615 |
| 0·2145 | 0·1287 | 0·6994 | 0·4162 | 1·499 | 1·051 | 2·589 | 2·328 | 3·506 | 3·750 |
| 0·3137 | 0·1844 | 0·7018 | 0·4174 | 1·674 | 1·228 | 2·678 | 2·456 | 3·898 | 4·406 |
| 0·3710 | 0·2157 | 0·8275 | 0·5011 | 1·888 | 1·508 | 3·039 | 2·995 | 4·086 | 4·730 |
| 0·4462 | 0·2615 | 0·8944 | 0·5485 | 2·177 | 1·791 | 3·064 | 3·041 | 4·286 | 5·082 |
| 0·5342 | 0·3091 | 0·9591 | 0·5988 | 2·194 | 1·808 | | | | |
| $UO_2{\cdot}SO_4$ | NaCl | $UO_2{\cdot}SO_4$ | NaCl | $UO_2{\cdot}SO_4$ | NaCl | $UO_2{\cdot}SO_4$ | NaCl | $UO_2{\cdot}SO_4$ | NaCl |
| 0·1132 | 0·06292 | 0·4570 | 0·2284 | 1·086 | 0·5895 | 2·386 | 1·705 | 4·605 | 4·226 |
| 0·1560 | 0·08389 | 0·5796 | 0·2917 | 1·251 | 0·7066 | 2·499 | 1·824 | 4·652 | 4·269 |
| 0·2265 | 0·1184 | 0·6542 | 0·3323 | 1·260 | 0·7129 | 2·776 | 2·117 | 5·317 | 5·022 |
| 0·2473 | 0·1257 | 0·6648 | 0·3364 | 1·346 | 0·7756 | 3·370 | 2·786 | 5·392 | 5·111 |
| 0·3261 | 0·1623 | 0·7405 | 0·3806 | 1·593 | 0·9711 | 3·373 | 2·786 | 5·983 | 5·726 |
| 0·3429 | 0·1703 | 0·8799 | 0·4630 | 1·789 | 1·137 | 3·466 | 2·893 | 6·069 | 5·806 |
| 0·3724 | 0·1849 | 1·063 | 0·5776 | 2·036 | 1·363 | 3·986 | 3·506 | 6·371 | 6·122 |

of measurements had to be made because it is not easy to plot the isopiestic ratio ($R = m_{NaCl}/m_{BeSO_4}$) against $m_{BeSO_4}$. Moreover, the values in the region of 0·1*m* are not of high accuracy because the concentrations of the reference salt, of the order of 0·05*m*, are not favourable to isopiestic measurements.

Since we know little about the activity coefficients of bivalent metal sulphates at concentrations below 0·1*m*, all activity coefficients have been calculated relative to an arbitrary

value of 0·150 at 0·1*m*. The values of the osmotic and activity coefficients at round concentrations are given in Table 2.

Beryllium sulphate behaves as might be expected: its activity coefficient is somewhat greater than that of magnesium sulphate as is consistent with the greater degree of hydration to be expected from the small radius of the beryllium ion (0·31 Å) in contrast to that of the magnesium ion (0·65 Å). Ion-pair formation must occur with both sulphates but should be less for beryllium sulphate because of hydration.

There is nothing about uranyl sulphate to distinguish it from other bivalent metal sulphates. To illustrate this, Table 2 includes values of the activity coefficient of manganese sulphate (Robinson and Stokes, *Trans. Faraday Soc.*, 1949, **45**, 612) which are of the same order as those of uranyl sulphate. Secoy's values for uranyl sulphate, also included, are in fair agreement with mine up to 1*m* but diverge considerably at higher concentrations and are of a different order of magnitude at 3·5*m*. This is not surprising because it is at these high concentrations that the correction to a uniform temperature is important. As a result of these experiments, I conclude that, although bivalent metal sulphates are undoubtedly complicated in behaviour, uranyl sulphate is no different from the others.

TABLE 2. *Osmotic and activity coefficients of beryllium sulphate and uranyl sulphate at 25°.*

| | $BeSO_4$ | | $UO_2 \cdot SO_4$ | | | $MnSO_4$ |
|---|---|---|---|---|---|---|
| *m* | $\phi$ | $\gamma$ | $\phi$ | $\gamma$ | $\gamma$ (Secoy) | $\gamma$ |
| 0·1 | 0·582 | (0·150) | 0·529 | (0·150) | (0·150) | (0·150) |
| 0·2 | 0·560 | 0·109 | 0·488 | 0·102 | 0·108 | 0·106 |
| 0·3 | 0·544 | 0·0885 | 0·463 | 0·0807 | 0·080 | 0·085 |
| 0·5 | 0·535 | 0·0692 | 0·462 | 0·0611 | 0·056 | 0·064 |
| 0·7 | 0·548 | 0·0600 | 0·470 | 0·0515 | 0·049 | 0·053 |
| 1·0 | 0·580 | 0·0530 | 0·495 | 0·0439 | 0·047 | 0·044 |
| 1·5 | 0·658 | 0·0491 | 0·557 | 0·0385 | 0·053 | 0·038 |
| 2·0 | 0·757 | 0·0497 | 0·628 | 0·0367 | 0·066 | 0·035 |
| 2·5 | 0·889 | 0·0538 | 0·710 | 0·0370 | 0·090 | 0·035 |
| 3·0 | 1·019 | 0·0613 | 0·792 | 0·0383 | 0·131 | 0·038 |
| 3·5 | 1·171 | 0·0724 | 0·873 | 0·0401 | 0·274 | 0·042 |
| 4·0 | 1·327 | 0·0875 | 0·951 | 0·0433 | — | 0·048 |
| 4·5 | — | — | 1·025 | 0·0465 | — | — |
| 5·0 | — | — | 1·092 | 0·0500 | — | — |
| 5·5 | — | — | 1·150 | 0·0536 | — | — |
| 6·0 | — | — | 1·198 | 0·0571 | — | — |

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## 884. *The Preparation of Alkylarylarsines.*

By FREDERICK G. MANN and BRYAN B. SMITH.

CRAGOE, ANDRES, COLES, ELPERN, MORGAN, and HAMILTON (*J. Amer. Chem. Soc.*, 1947, **69**, 925) prepared methylphenylarsine by converting phenyldichloroarsine by the Meyer reaction into methylphenylarsinic acid, followed by reduction to the arsine, which is apparently the only alkylarylarsine hitherto recorded. For the preparation of a series of such arsines, it is advantageous to reduce phenylarsonic acid to phenylarsine and convert the latter in liquid ammonia into the monosodium derivative, PhAsNaH, which reacts readily with alkyl halides to give the alkylphenylarsine: only one reduction is thus required.

*Experimental.*—Liquid ammonia (200 c.c.) was placed in a flask fitted with a 3-necked adaptor carrying a mercury-sealed stirrer, a dropping funnel, and an exit tube packed with

cotton wool to prevent inward diffusion of air. Sodium (1·8 g., 1·1 mols.), cut into small pieces, was dissolved in the stirred ammonia, and phenylarsine (8 c.c., 1 mol.) in dry ether was then added dropwise, the blue colour of the solution changing to golden-yellow when the addition was complete. The alkyl bromide (1·1 mols.) was then slowly added, and after a few minutes' stirring the solution became colourless. The ammonia was allowed to evaporate, and all the volatile residue was distilled off at 14 mm. without fractionation. The distillate was then carefully fractionated in nitrogen under reduced pressure. The following arsines were colourless liquids which underwent rapid oxidation on exposure to air: *Ethylphenylarsine* (31% yield), b. p. 86·5—87·5°/14 mm. (Found: C, 52·65; H, 5·85. $C_8H_{11}As$ requires C, 52·75; H, 6·1%). *Phenyl*-n-*propylarsine* (51% yield), b. p. 96—97°/12 mm. (Found: C, 55·5; H, 6·8. $C_9H_{13}As$ requires C, 55·1; H, 6·7%). n-*Butylphenylarsine* (68% yield), b. p. 117°/15·5 mm. (Found: C, 57·0; H, 7·1. $C_{10}H_{15}As$ requires C, 57·15; H, 7·2%). The progressive rise in yield throughout this series is probably partly due to the decreasing volatility of the alkyl bromides; a portion of the ethyl bromide in particular may have been swept out of the apparatus by the stream of ammonia gas. Furthermore, these yields could doubtlessly be increased by working on a larger scale.

It is probable that these arsines in liquid ammonia solution will react with a second equivalent of sodium. When the quantities of sodium and of ethyl bromide in the above experiment were doubled, distillation gave diethylphenylarsine, b. p. 100·5—101°/11 mm., in 34% yield: it was identified by combination with cold methyl iodide, followed by conversion into diethylmethylphenylarsonium picrate, m. p. 85—86° unchanged by admixture with an authentic sample (cf. Beeby and Mann, *J.*, 1951, 890).

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## 885. *Quinaldinoyl Chloride.*

By D. LL. HAMMICK and A. M. ROE.

A SUBSTANCE described as quinaldinoyl chloride was first prepared by Meyer (*Monatsh.*, 1904, **25**, 1199; *Ber.*, 1905, **38**, 2488) by the action of thionyl chloride on quinaldinic acid. He described it as a very sparingly soluble, crystalline substance of m. p. 175—176°. Besthorn and Ibele (*Ber.*, 1905, **38**, 2127) claimed to have obtained, by the same reaction, an acid chloride of m. p. 96°, readily soluble in organic solvents. Meyer's inability to obtain Besthorn's product was ascribed by Besthorn (*Ber.*, 1908, **41**, 2003) to the presence of anticatalysts (notably tin) in the thionyl chloride used. It was suggested, in a long and inconclusive controversy summarised by Meyer and Turnau (*Ber.*, 1909, **42**, 1163), that the high-melting compound was a polymeric form of quinaldinoyl chloride.

Preparation of the lower-melting chloride was not recorded again until Hammick and Dickinson (*J.*, 1929, 214) made it by the action of phosphorus pentachloride on pure dry quinaldinic acid in ligroin (cf. also Krollpfeiffer and Schneider, *Annalen*, 1937, **530**, 34). However, the preparation requires not only absolutely dry quinaldinic acid, but also freshly distilled ligroin dried over sodium.

Spath and Spitzer (*Ber.*, 1926, **59**, 1480) suggested that the substance, m. p. 175—176°, might be the hydrochloride of quinaldinic acid. In the present note we adduce evidence that confirms this.

First, analyses agree with this requirement (Found: C, 57·3, 56·7; H, 3·8, 4·0; N, 6·7, 7·0; Cl, 16·9, 17·1. Calc. for $C_{10}H_8O_2NCl$: C, 57·2; H, 4·3; N, 6·45; Cl, 16·7. Calc. for $C_{10}H_6ONCl$: C, 62·7; H, 3·1; N, 7·3; Cl, 18·55%). Secondly, crystallisation from dry *cyclo*hexanone gave fine needles, m. p. 153° (decomp.), undepressed on admixture with quinaldinic acid. Thirdly, a specimen of quinaldinic acid hydrochloride, m. p. 177·5—181° (decomp.), prepared by crystallisation of quinaldinic acid from hydrochloric acid (25%), gave a mixed m. p. of 179—179·5° with the high-melting "chloride" (owing to the decomposition, no very firm conclusions can be drawn from these figures).

The infra-red absorption peaks for quinaldinic acid and the low- and the high-melting chloride (taken in a paraffin paste) leave the matter in no doubt (see Table). They

show that quinaldinic acid exists as a zwitterion in the solid state; this is confirmed by Flett (*J.*, 1951, 962), and provides a useful confirmation of the fact that this acid can be decarboxylated in polar solvents as the zwitterion (Brown and Hammick, *J.*, 1949, 659).

| Compound | Max. ($\mu$) | | | |
|---|---|---|---|---|
| Quinaldinic acid ..... | — | 5·18 medium, broad | — | |
| High-melting " chloride " (hydrochloride) ..... | 3·08 medium | 5·05 strong, broad | 5·82 strong | |
| Low-melting acid chloride ..... | — | 5·05 weak, broad | 5·70 strong | 5·82 weak |

The absorption of the high-melting form indicates the presence of a hydroxyl (3·08 $\mu$) and a carbonyl bond (5·82 $\mu$). The genuine acid chloride shows no hydroxyl and has a carbonyl absorption at 5·70 $\mu$ as expected; it shows to a small degree the absorption of the high-melting material, and analysis of the same sample showed that partial hydrolysis had indeed occurred. The broad absorption shown by the above quinaldinium compounds near 5·1 $\mu$, may be associated with the structure $-\overset{+}{N}H{:}C<$ (cf. Randall, Fowler, Fuson, and Dangle, " Infra-red Determination of Organic Structures," Van Norstrand, New York, 1949, for amino-acids and amino-acid hydrochlorides).

We record also that we have isolated, from the residue obtained after refluxing pure quinaldinic acid with phosphorus pentachloride in ligroin, the hydrochloride of Besthorn's Red (Krollpfeiffer and Schneider, *loc. cit.*). Work on this and analogous compounds will be reported later.

We thank Dr. F. B. Strauss for measuring the infra-red absorptions and for helpful discussions.

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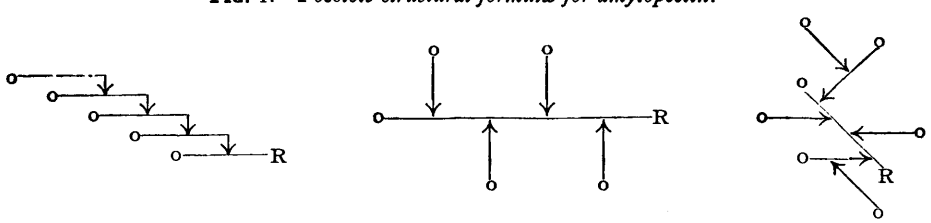
## 886. *Evidence of Multiple Branching in Waxy Maize Starch.*

BY STANLEY PEAT, W. J. WHELAN, and GWEN J. THOMAS.

THREE structural formulæ have been suggested for amylopectin, *viz.*, the Haworth laminated formula, Fig. 1*a* (Haworth, Hirst, and Isherwood, *J.*, 1937, 577), the Staudinger " comb " formula, Fig. 1*b* (Staudinger and Husemann, *Annalen*, 1937, **527**, 195), and the Meyer arborescent formula, Fig. 1*c* (Meyer and Bernfeld, *Helv. Chim. Acta*, 1940, **23**, 865). Hitherto little experimental evidence has been forthcoming to distinguish between the three methods of branching since each appeared adequately to explain the known facts.

FIG. 1. *Possible structural formulæ for amylopectin.*




(*a*) Haworth. (*b*) Staudinger. (*c*) Meyer.

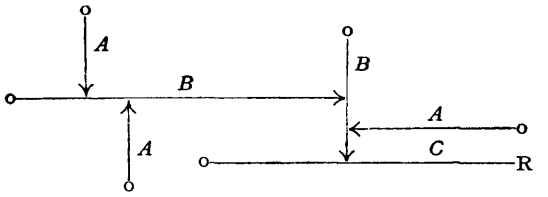
o = Non-reducing chain end, ↓ = α-1 : 6-Link, R = Free reducing chain end.

The essential differences may be expressed in the following terms. The Haworth formula represents a series of short linear chains (containing an average of 25 glucose units joined by α-1 : 4-links) mutually connected by α-1 : 6-glucosidic branch linkages in which the

***average*** position of the branch link is at the centre of the repeating chains. This laminated formula implies a system of single branching and it differs from Meyer's formula in that the latter envisages multiple and random branching of the chains (Fig. 1*c*). The Staudinger and Haworth formulæ represent extremes, inasmuch as in the former all the branch links are carried by a single main chain.

It will be observed that three arrangements of the basal (linear) chains are possible; these are represented by chains *A*, *B*, and *C* in Fig. 2. The interlinking of a chain with one

FIG. 2. *Types of chains in amylopectin.*




or more other chains involves the reducing group ($C_{(1)}$) and/or primary hydroxyl groups ($C_{(6)}$) of the constituent glucose members. In a type *A* chain only the $C_{(1)}$ group is engaged and in a type *C*, only $C_{(6)}$ groups. The attachment of a type *B* chain is however effected through its $C_{(1)}$ group and also through one or more of its $C_{(6)}$ groups. In each amylopectin molecule there will be only one chain of the third type, *C*, since this carries the sole reducing end group. Each structure given in Fig. 1 contains one *C* chain but they are distinguishable in respect of the proportions of *A* and *B* chains. In the Haworth formula there is only one *A* chain per molecule whereas the Meyer formulation requires many *A*, as well as *B*, chains. The Staudinger structure contains, in addition to the *C* chain, only *A* chains; it contains no *B* chains. It follows that if the proportion of *A* chains in the amylopectin structure could be determined, a distinction between these rival formulations becomes possible. A method for the detection of *A* chains has now been developed from our enzymic studies.

Waxy maize starch (amylopectin) was hydrolysed to the limit with dilute crystalline β-amylase, maltose was removed by dialysis, and the limit β-dextrin isolated. This dextrin (4·19 g.) was treated with the debranching R-enzyme (Hobson, Whelan, and Peat, *J.*, 1951, 1451). The dialysable portion of the product (1·77 g.) was fractionated on a charcoal–Celite column (Whistler and Durso, *J. Amer. Chem. Soc.*, 1950, **72**, 677; Bailey, Whelan, and Peat, *J.*, 1950, 3692). Glucose was not detected but maltose (0·278 g.; $0{\cdot}813 \times 10^{-3}$ mole) and maltotriose (0·282 g.; $0{\cdot}563 \times 10^{-3}$ mole) were obtained. The next product in order of increasing molecular weight was maltohexaose and this was followed by a continuous series of higher dextrins; maltotetraose and maltopentaose were not formed. Our interpretation of these results is as follows. Chains of type *A* will give rise, after the successive actions of dilute β-amylase and R-enzyme, to maltose or maltotriose according to whether they originally contained even or odd numbers of glucose units. Some of the *A* chains may of course consist initially of only two or three glucose units. Since the 4- and the 5-unit maltodextrins are not found among the products of debranching of limit β-dextrin, the length of the *B* chains in the β-dextrin (and therefore in the amylopectin) cannot be less than six glucose units. In other words, the maltose and maltotriose isolated as products of debranching can have come only from the *A* chains and not from the *B* chains.

Maltose and maltotriose were liberated by R-enzyme from the β-dextrin in the molar ratio, 1·45 : 1, although it might have been expected that equimolar quantities of these sugars would result, since the chances of an *A* chain containing an even or an odd number of glucose units are presumably equal. The discrepancy is possibly due to the incomplete removal of maltose during the initial dialysis of the β-dextrin. If 1·9% of the maltose produced by β-amylase had remained in the β-dextrin this discrepancy would be explained. It should be noted that the maltotriose is a product only of the debranching action of R-enzyme; it is not liberated by β-amylase acting alone on amylopectin.

If the laminated formula (Fig. 1*a*), having a single *A* chain, represents the structure of amylopectin, then the β-dextrin derived from it would yield, when debranched by R-enzyme, equimolar amounts of maltose amd maltotriose, corresponding to an average of 2·5 glucose residues per molecule. The actual molecular size of waxy maize β-dextrin has not been determined but since the results of Potter and Hassid (*J. Amer. Chem. Soc.*, 1948, **70**, 3774) indicate a variation between 6000 and 37,000 glucose residues per molecule for a number of amylopectins of plant origin the lower limit of 6000 may be taken as a minimum value for waxy maize starch. Since β-amylase removes about 50% of the molecule as maltose, it may be further assumed that the degree of polymerisation of the β-dextrin is at least 3000. The molar percentage of maltose + maltotriose to be expected from the Haworth model β-dextrin would therefore be 0·083. The actual yield was however much greater, namely, 5·3%. Clearly the proportion of *A* type chains is far higher than is implied by the laminated formula. It must be concluded that *multiple* branching is an intrinsic part of the amylopectin structure. The Staudinger formulation (Fig. 1*b*) must also be incorrect, since all the chains in it except one are of the *A* type and calculation shows that the proportion of maltose + maltotriose liberated by R-enzyme from the β-dextrin would be of the order of 25%. (The basal repeating chain of waxy maize starch contains an average of 20 glucose units; Brown, Halsall, Hirst, and Jones, *J.*, 1948, 27.) Accordingly, the multiple and random branching of Meyer's model (Fig. 1*c*) is favoured, since it implies a submaximal proportion of *A* chains.

Attention is drawn to the fact that the α-1 : 6-glucosidic linkage terminating an *A* chain at its potential reducing end does not interfere with the normal course of β-amylolysis except that the ultimate maltose or maltotriose unit remaining after the action of β-amylase on amylopectin (Fig. 2) would be part of the β-dextrin molecule. It may be that the linked 3-unit chain so produced is further degraded with the liberation of maltose by the prolonged action of a concentrated solution of β-amylase, as is maltotriose (Bailey, Whelan, and Peat, *J.*, 1950, 3692). This possibility is being investigated. [Added in proof, Oct. 9th, 1952: See Larner and Cori, *Chem. Eng. News*, 1952, **30**, 1524.]

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