NOTES.

Colour Tests. Part II. A Characteristic Test for 2-Methyl-4-pyrones.*

By Alexander Schönberg and Aly Sina.

The colour reaction of certain 4-pyrones with potassium hydroxide (Schönberg and Sina, *J. Amer. Chem. Soc.*, 1950, **72**, 1611) has now been studied in detail. Only 2-methyl-4-pyrones not containing a phenolic hydroxyl group give a positive reaction (red-violet colour). Derivatives of 2-ethyl- and 2-propyl-chromone may develop other colours. The test is suitable for use on the micro-scale.

The result of the test is independent of the presence of oxygen, whilst the violet products are stable only in very concentrated alkaline medium, in which they are not very soluble and form flocculent precipitates. On the addition of a large amount of ice-water the colour disappears in about 2 minutes, with regeneration of the original 2-methyl-4-pyrone (possibly with small amounts of hydrolysis products). Some compounds enumerated in the table, *e.g.*, khellin, were tested by using barium hydroxide instead of potassium hydroxide, but no colour was produced.

Experimental.—The test was carried out as previously described (Schönberg and Sina, *loc. cit.*). Compounds sparingly soluble in water were dissolved in 50% alcohol. With 2-methyl-5 : 6-benzchromone, which is very sparingly soluble in cold alcohol, the test was carried out as follows: potassium hydroxide pellets were placed in a glass evaporating dish on a boiling-water bath for 2 minutes; then, without removal of the dish, a hot solution of the chromone (10 mg.) in *n*-propyl alcohol (2 c.c.) was added; a red-violet colour developed within ½ minute.

Compounds giving a positive test.

2 : 6-Dimethylpyrone.[6]
3-Chloro-2 : 6-dimethylchromone.[1]
6-Chloro-2 : 3-dimethylchromone.[1]
2 : 3-Dimethylchromone.[1, 6]
2 : 6-Dimethylchromone.
2 : 7-Dimethylchromone.
7-Methoxy-2-methylchromone.[6]
6-Chloro-2-methyl-3-ethylchromone.[1]
2 : 3 : 7-Trimethylchromone.[1]
7-Ethoxy-2-methylchromone.[6]
7 : 8-Dimethoxy-2-methylchromone.[6]
Visnagin (natural and synthetic).[5, 6, 7]
2 : 7-Dimethyl-3-ethylchromone.[1]
7-Propoxy-2-methylchromone.[6]
2-Methyl-5 : 6-benzchromone.[2]
Khellin.[5, 6]
5 : 8-Diethoxy-2-methylfurano(3′ : 2′-6 : 7)chromone.[7]
5 : 8-Dicarbomethoxy-2-methylfurano(3′ : 2′-6 : 7)chromone.[7]

Compounds giving a negative test.

Kojic acid.[4]
Chromone.[6, 7]
3-Methylchromone.
6-Methylchromone.[6]
7-Hydroxy-2-methylchromone.
Norvisnagin.[7]
5 : 8-Dihydroxy-3-methylfurano(3′ : 2′-6 : 7)chromone.[7]
6-Chloro-3-methyl-2-ethylchromone.[1, 3]
Norkhellin.[6]
2-Ethylnorvisnagin.[3, 5, 7]
Flavone.
2-Ethylnorkhellin.[3, 6]
2-Benzylchromone.
2-*n*-Propylnorkhellin.[3, 6]
7 : 8-Benzflavone.
2-Phenylnorkhellin.[6]
2-Benzylnorkhellin.
2 : 3-Dimethylchromone oxime.
2-Styryl derivative of khellin.[6]
3-Benzyl-2-*p*-methoxystyryl-7′-methylchromone.

[1] In 50% alcohol. [2] In *n*-propyl alcohol. [3] The compound gives a weak brownish-red colour. [4] The compound gives an orange colour which faded quickly. [5] The products of alkaline hydrolysis of this γ-pyrone do not give the colour test. [6] Schönberg and Sina, *loc. cit.* [7] Schönberg and Sina, *J. Amer. Chem. Soc.*, 1950, **72**, 3396.

Stability of the violet compounds obtained from khellin and from 2 : 6-dimethylpyrone. A test-tube (15 × 1·5 cm.) was one-third filled with potassium hydroxide pellets, and a solution of the 4-pyrone (0·01 g.) in water (2 c.c.) was poured in. A deep-violet precipitate was formed (slowly with 2 : 6-dimethylpyrone and almost immediately with khellin). When the tube was sealed this colour persisted for more than two weeks; with 2 : 6-dimethylpyrone it gradually became brownish-violet.

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* *J.*, 1949, 766 is considered to be Part I of this series.

Regeneration of khellin from the violet reaction product with potassium hydroxide. Finely powdered khellin (0·2 g.), suspended in water (4 c.c.), was added to potassium hydroxide pellets (20 g.), and the mixture shaken for 3 minutes without cooling. The violet deposit was collected on a wide sintered-glass funnel, quickly covered with dry ether, transferred to a dry mortar containing dry ether, and pulverised under dry ether. The supernatant ether was decanted off and the solid again washed with ether. The violet compound in dry ether (30 c.c.) was shaken with ice-water (20 c.c.), and the ethereal layer was separated, and after being washed with water was evaporated to dryness, leaving a residue (0·03 g.) of khellin (m. p. and mixed m. p.). The yield was low as no attempt was made to recover the violet product adhering to the potassium hydroxide pellets. The aqueous layer on acidification with hydrochloric acid did not give a deposit and its yellow colour persisted.

Preparation of 3-*methylchromone.* *o*-Hydroxypropiophenone (6 g.) was dissolved in warm ethyl formate (25 c.c.), and an ethereal suspension of powdered sodium (4·5 g.) gradually added, the vigorous reaction being controlled by external cooling when necessary. When the reaction had subsided, more ester (10 c.c.) and then powdered sodium (1 g.) were added, and the mixture was heated under reflux for 10 minutes. Next day, ice and water were carefully added and the resulting alkaline solution was washed twice with ether, and, after removal of traces of this solvent, acidified with acetic acid. The product was extracted with ether, washed with water, and dried (Na_2SO_4). The oily residue obtained on evaporation of the ether was dissolved in concentrated sulphuric acid (8 c.c.), and after 15 minutes this solution was diluted with ice-water. The 3-methylchromone recrystallised from a mixture of a small amount of acetone and much light petroleum (b. p. 60—80°) and then from light petroleum, as colourless crystals, m. p. 69°. Difficulty was experienced in preparing this chromone by Mentzer and Meunier's method (*Bull. Soc. chim.*, 1944, [v], **11**, 302), who gave m. p. 68°.

Preparation of 2-*benzylnorkhellin.* Khellinone (Spāth and Gruber, *Ber.*, 1938, **71**, 106) (4 g.) was dissolved in ethyl phenylacetate (20 g.) and condensed by gradual addition of powdered sodium (2·5 g.) in dry ether as described above. The oily diketone obtained on acidification with dilute hydrochloric acid, thickened when kept, and was separated by decantation, washed with water, pressed, and then washed with light petroleum (b. p. 60—90°), whereupon it solidified; the solid crystallised from methyl alcohol as a yellowish crystalline compound, which was heated under reflux with alcoholic sulphuric acid (30%) for 30 minutes, and the solution diluted with water and neutralised with sodium carbonate. The separated solid was washed with water and crystallised twice from alcohol and finally from benzene; it formed almost colourless crystals, m. p. 148° (Found : C, 71·2; H 4·8. $C_{20}H_{16}O_5$ requires C, 71·4; H, 4·8%). Sulphuric acid gave an orange solution.

Preparation of 7 : 8-*dimethoxy*-2-*methylchromone.* 2-Hydroxy-3 : 4-dimethoxyacetophenone (David and Kostanecki, *Ber.*, 1903, **36**, 125) (2 g.) was condensed with ethyl acetate (8 c.c.) in the presence of powdered sodium (2 g.) as previously described. The product, after extraction with ether and cyclisation as above, yielded 7 : 8-dimethoxy-2-methylchromone, which after recrystallisation from light petroleum (b. p. 60—80°) had m. p. 102°. Blumberg and Kostanecki (*Ber.*, 1903, **36**, 2191) give m. p. 102°.

The authors are indebted to Mr. R. Azzam for a gift of some chemicals.—Fouad I University, Faculty of Science, Cairo, Egypt. [*Received, June* 5*th*, 1950.]

The Condensation of Aromatic Amines with Ethyl α-Chloro-α-formylacetate.

By D. A. H. Taylor.

Mentzer (*Compt. rend.*, 1946, **222**, 1176) states that when ethyl α-chloro-α-formylacetate is heated with aniline, a substance, m. p. 82°, is formed, to which he ascribes the structure ethyl indole-3-carboxylate. The author required indole-3 : 4-dicarboxylic acid, and Mentzer's method seemed to present a convenient one for preparing it. However, when two molecular proportions of methyl *m*-aminobenzoate and one of ethyl chloroformylacetate were heated at 190° in an oil-bath, the reaction was very different in character from that between chloroacetone and aniline. Water was seen to be lost, but the mixture remained pale in colour, and no exothermic reaction occurred. On cooling and scratching the product under dilute hydrochloric acid, it crystallised readily, and on recrystallisation from benzene had m. p. 136°. Analysis showed, however, that it was not the expected product, but ethyl (*m*-carbomethoxyanilinomethylene)chloroacetate (I).

$$m\text{-}MeO_2C{\cdot}C_6H_4{\cdot}NH{\cdot}CH{:}CCl{\cdot}CO_2Et$$

(I.)

Repetition of Mentzer's work with aniline and *p*-toluidine gave compounds agreeing in melting point with those which he records, but of which the analyses agree with structures analogous to (I). The only analysis which Mentzer quotes is a nitrogen value for the *p*-toluidine derivative, and this agrees equally well with both structures. Evidently the halogen atom in the ester is not sufficiently reactive to react with aniline, which is usually the first stage of the synthesis of indoles from halogenated ketones. This is in agreement with the fact that chloroformylacetic ester is not lachrymatory.

Experimental.—*Ethyl* (m-*carbomethoxyanilinomethylene*)*chloroacetate.* Methyl *m*-aminobenzoate (38 g., 0·2 mol.) and ethyl α-chloro-α-formylacetate (15 g., 0·1 mol.) were heated in an oil-bath at 190° for 15 minutes. After cooling, water (100 ml.) and concentrated hydrochloric acid (20 ml.) were added, the mixture stirred for a few minutes, and the precipitate filtered off and dried. Crystallisation from benzene gave *ethyl* (m-*carbomethoxyanilinomethylene*)*chloroacetate* (23 g., 80%), which formed pale-tan crystals, m. p. 136° (Found : C, 55·1; H, 4·85; N, 4·7. $C_{13}H_{14}O_4NCl$ requires C, 55·1; H, 4·9; N, 4·9%).

Ethyl (*anilinomethylene*)*chloroacetate.* This was prepared by Mentzer's method for the substance which he describes as ethyl indole-3-carboxylate; it formed crystals, m. p. 82° (Mentzer gives m. p. 82°) (Found : Cl, 15·3. Calc. for $C_{11}H_{12}O_2NCl$: Cl, 15·5%).

Ethyl α-*chloro*-p-*methylanilinomethyleneacetate* was prepared similarly (preparation by Mr. J. E. Saxton). It formed flat plates, m. p. 97° (Found : C, 59·8; H, 6·1; N, 5·6; Cl, 13·9. Calc. for $C_{12}H_{14}O_2NCl$: C, 60·1; H, 5·85; N, 5·85; Cl, 14·8%) (Mentzer gives m. p. 97°; Found : N, 6·2. Calc. for $C_{12}H_{13}O_2N$: N, 6·9%).

Analyses are by Drs. Weiler and Strauss.—DYSON PERRINS LABORATORY, OXFORD. [*Received, June 26th*, 1950.]

The Purification of Benzene. By R. F. EVANS, O. ORMROD, B. B. GOALBY, and L. A. K. STAVELEY.

WHEN benzene is shaken with an ammoniacal solution of nickel cyanide, a pale violet crystalline solid of formula $Ni(CN)_2,NH_3,C_6H_6$ (Hofmann and Höchtlen, *Ber.*, 1903, **36**, 1149) separates. The structure of this solid has recently been investigated by Powell and Rayner (*Nature*, 1949, **163**, 566), who found that it is an example of the clathrate type of molecular compound. Thiophen, furan, and pyrrole can also form similar solids, but aniline and phenol seem to be the only simple derivatives of benzene itself capable of replacing benzene in the complex. Since all these organic molecules are flat, it seemed probable that if the benzene compound were formed from thiophen-free but otherwise impure benzene, the benzene recovered on the destruction of the compound should be quite free from the saturated hydrocarbons which are otherwise very difficult to remove. We have, in fact, found that by this method benzene can be obtained from impure material in good yield and of a purity as good as, if not superior to, that of samples produced by prolonged fractionation in a very efficient still, or by the tedious and wasteful process of fractional crystallisation and fusion.

In a preliminary experiment, the compound was formed by using an ammoniacal nickel cyanide solution prepared as recommended by Dennis and Nichols ("Gas Analysis," Macmillan, 1929), and a sample of impure benzene which was sulphur-free and froze at 4·55°. The solid was washed with water and acetone, and then heated in a boiling saturated solution of potassium chloride, the benzene distilling over. This benzene, after being washed with water, dilute acid, and dilute sodium carbonate, dried, and distilled from phosphoric oxide, had an initial f. p. of 5·4°. This demonstrated the feasibility of the method, but as the solid had only been produced in quantity by continued agitation for at least 24 hours, further experiments were made to find conditions under which it was formed more quickly, and alternative methods of recovering the benzene from the complex were tried, of which the best was found to be dry distillation of the solid from an oil-bath at 190—210°. The most satisfactory procedure for the formation of the solid may be illustrated by the following experiment.

A cold solution of 70·6 g. of potassium cyanide in 282 c.c. of water was added with stirring to a cold solution of 120 g. of hydrated nickel chloride in 480 c.c. of water (or to one of 142 g. of hydrated nickel sulphate in 567 c.c. of water). After addition of 564 c.c. of concentrated aqueous ammonia and 300 c.c. of water, and 30 minutes' standing in ice, the mixture was filtered through glass-wool. 60% Aqueous acetic acid was added to the filtrate until a turbidity appeared. 32·6 g. of benzene were then added to the solution, which was vigorously shaken for one hour and then cooled in ice for the same time. The solid complex was filtered off, washed with water, alcohol, and ether, and air-dried, a 94% yield being obtained. On dry distillation of the complex, 24·5 g. of benzene were recovered, representing an overall yield of 75%.

Starting from sulphur-free benzene with an initial f. p. of 5·40°, a quantity of benzene was prepared in this way. After being washed three times with 20% sulphuric acid, and then with water, this was dried over phosphoric anhydride and fractionated in a 25-plate column. The purity of the constant-boiling middle fraction (which constituted about 77% of the whole) was then examined; it had n_D^{20} 1·5011, d_4^{20} 0·87904. Finally, its behaviour on freezing was investigated in an apparatus similar to that described by Mair, Glasgow, and Rossini (*J. Res. Nat. Bur. Stand.*, 1941, **26**, 591), temperature being measured with a Meyers-type platinum resistance thermometer. This thermometer, the characteristics of which satisfied the requirements of the International Temperature Scale, had been checked at the transition point of sodium sulphate, for which a value of 32·381° was found (cf. 32·384°; Dickinson and Mueller, *ibid.*, 1907, **3**, 641). The rate of fall of temperature after freezing commenced was so small (less than 0·02° in 30 minutes) as to make it difficult to apply Taylor and Rossini's procedure (*ibid.*, 1944, **32**, 197) for obtaining the f. p. of the perfectly pure substance. The extrapolated value of the initial f. p. of the actual sample, however, was 5·535°, as compared with the value of 5·533°, estimated to be the f. p. of pure benzene ("Selected Values of the Properties of Hydrocarbons," U.S. Nat. Bur. Standards, 1947). It therefore appears that the method described can be used to obtain benzene from the commercial product in good yield and of high purity, without using any particularly elaborate apparatus.

One of us (R. F. E.) is indebted to the Department of Scientific and Industrial Research for a Maintenance Grant, and another (B. B. G.) to the British Rayon Research Association for a Research Scholarship.—THE INORGANIC CHEMISTRY LABORATORY AND DYSON PERRINS LABORATORY, OXFORD. [*Received, July 3rd*, 1950.]

The Bromination of Halogenoacetals. By G. T. NEWBOLD.

THE preparation of dibromoacetaldehyde diethyl acetal by the bromination of bromoacetal in the presence of calcium carbonate by Hartung and Adkins's method (*J. Amer. Chem. Soc.*, 1927, **49**, 2517; cf. Fischer and Landsteiner, *Ber.*, 1892, **25**, 2551; von Braun, *Ber.*, 1902, **35**, 3388; Freundler and Ledru, *Compt. rend.*, 1905, **140**, 794; *Bull. Soc. chim.*, 1907, [iv], **1**, 75) has been described by Beyerstadt and McElvain (*J. Amer. Chem. Soc.*, 1937, **59**, 2266). In the author's hands this preparation consistently gave a crystalline by-product, $C_8H_{14}O_3Br_4$. This is formulated as di-(2 : 2-dibromo-1-ethoxyethyl) ether (I) since on treatment with methanolic 2 : 4-dinitrophenylhydrazine sulphate it gives glyoxal bis-2 : 4-dinitrophenylhydrazone. The ready conversion of dibromoacetal into the same hydrazone under these conditions is an indication of the lability of the two bromine atoms and supports the above formulation of the compound $C_8H_{14}O_3Br_4$. Attempts to form the 2 : 4-dinitrophenylhydrazone of dibromoacetaldehyde also resulted in the formation of glyoxal bis-2 : 4-dinitrophenylhydrazone. Catalytic reduction of (I) followed by treatment with 2 : 4-dinitrophenylhydrazine in acid solution, without isolation of the intermediate di-(1-alkoxyethyl) ether (cf. Geuther and Laatsch, *Annalen*, 1883, **218**, 25), gave acetaldehyde 2 : 4-dinitrophenylhydrazone.

Further support for the structure (I) was forthcoming from certain reactions of di-(1 : 2-dibromoethyl) ether (II) (for preparation see Freundler, *Compt. rend.*, 1905, **140**, 1693, and *Bull. Soc. chim.*, 1907, [iv], **1**, 66; for structure, see Hibbert, Perry, and Taylor, *J. Amer. Chem. Soc.*, 1929, **51**, 1551, and Stepanow, Preobrashensky, and Schtschukina, *Ber.*, 1926, **59**, 2533). Ruigh and Major (*J. Amer. Chem. Soc.*, 1931, **53**, 3131) showed that (II) gave glyoxal bis-*p*-nitrophenylhydrazone on treatment with a hot solution of *p*-nitrophenylhydrazine in aqueous acetic acid, by fission of the ether linkage and concomitant hydrolysis and oxidation at the 2-position.

Di-(1 : 2-dibromoethyl) ether was isolated as a by-product of the bromination of paraldehyde followed by addition of ethanol. In contrast to the behaviour with *p*-nitrophenylhydrazine reported above, this ether with Brady's reagent in the cold gives bromoacetaldehyde 2 : 4-dinitrophenylhydrazone in excellent yield; fission of the oxygen linkage in this case would appear easier than hydrolysis of the acetal groups in bromoacetal since the latter compound gave with Brady's reagent a mixture of bromoacetaldehyde 2 : 4-dinitrophenylhydrazone and glyoxal bis-2 : 4-dinitrophenylhydrazone, the formation of the latter involving an oxidation.

Bromination of chloroacetal in the presence of calcium carbonate gave bromochloroacetal and in small yield a product, $C_8H_{14}O_3Br_2Cl_2$. This compound was degraded by Brady's reagent to glyoxal bis-2 : 4-dinitrophenylhydrazone and is formulated as di-(2-bromo-2-chloro-1-ethoxyethyl) ether (III).

$$[CHBr_2{\cdot}CH(OEt){\cdot}]_2O \quad (CH_2Br{\cdot}CHBr)_2O \quad [CHBrCl{\cdot}CH(OEt)]_2O$$

(I.) (II.) (III.)

Experimental.—All m. p.s are uncorrected.

Bromination of bromoacetal. To bromoacetal (565 g.), stirred with dry precipitated calcium carbonate (165 g.), bromine (468 g.) was added at 0° during 2 hours in strong sunlight. Stirring was continued for a further hour. Next morning ice-water was added, and the lower layer separated, washed with potassium carbonate solution, then water, and dried (Na_2SO_4). Distillation gave a forerun, b. p. 60—95°/11 mm. (150 g.), followed by dibromoacetal, b. p. 96—100°/11 mm. (490 g.), n_D^{19} 1·4850. The residue (40 g.) solidified on cooling. Two crystallisations from benzene–light petroleum (b. p. 60—80°) gave *di-*(2 : 2-*dibromo-*1-*ethoxyethyl*) *ether* (8·5 g.) as fine needles, m. p. 92—94° [Found : C, 20·1; H, 2·9; Br, 67·0%; *M* (cryoscopic in C_6H_6), 452. $C_8H_{14}O_3Br_4$ requires C, 20·1; H, 2·9; Br, 66·9%; *M*, 478].

Bromination of chloroacetal. Chloroacetal (250 g.) was brominated as above with bromine (285 g.) in the presence of calcium carbonate (96 g.). Distilllation of the product gave *bromochloroacetal* (190 g.), b. p. 46—50°/0·3 mm., n_D^{19} 1·4610 (Found : C, 30·8; H, 4·9. $C_6H_{12}O_2BrCl$ requires C, 31·1; H, 5·2%). The distillation residue (21 g.) solidified on cooling and after two crystallisations from light petroleum (b. p. 60—80°) gave *di-*(2-*bromo-*2-*chloro-*1-*ethoxyethyl*) *ether* as fine needles (4·9 g.), m. p. 89—91° [Found : C, 24·8; H, 3·8; Br + Cl, 60·1; *M* (cryoscopic in C_6H_6), 393. $C_8H_{14}O_3Br_2Cl_2$ requires C, 24·7; H, 3·6; Br + Cl, 59·4%; *M*, 389].

Reaction of di-(2 : 2-*dibromo-*1-*ethoxyethyl*) *ether with Brady's reagent.* The reagent used contained 2 : 4-dinitrophenylhydrazine (2 g.) in concentrated sulphuric acid (4 c.c.) and methanol (60 c.c.). A mixture of the ether in warm methanol (2 c.c.) and the reagent (5 c.c.) was kept at room temperature overnight and then heated at 60° for 30 minutes; the solid (80 mg.) was separated after cooling, washed with methanol, and crystallised from ethylene glycol monoethyl ether, giving orange needles, m. p. 320° (decomp.) (Found : C, 40·1; H, 2·7; N, 27·1. Calc. for $C_{14}H_{10}O_8N_8$: C, 40·2; H, 2·4; N, 26·8%). Light absorption in chloroform : inflection at 2600 A. (ε = 14,000), maxima at 3950 (ε = 34,000) and 4400 A. (ε = 36,000). Glyoxal bis-2 : 4-dinitrophenylhydrazone, prepared according to Glasstone and Hickling (*J.*, 1936, 820), separated from ethylene glycol monoethyl ether or nitrobenzene as small orange needles, m. p. 319·5° (decomp.) undepressed when mixed with the preparation described above (Found : N, 27·0%) (light absorption as above).

Reaction of di-(2-*bromo-*2-*chloro-*1-*ethoxyethyl*) *ether with Brady's reagent.* The compound (100 mg.), treated as above, gave glyoxal bis-2 : 4-dinitrophenylhydrazone (70 mg.), m. p. 320° (decomp.) alone or mixed with an authentic specimen (Found : C, 40·1; H, 2·6; N, 27·4%) (light absorption as above).

Reaction of dibromoacetal with Brady's reagent. Dibromoacetal (500 mg.) in methanol (2 c.c.) was mixed with the reagent (10 c.c.) and kept at room temperature. After 4 days the solid (190 mg.) was collected. It crystallised from ethylene glycol monoethyl ether as orange needles, m. p. 320° (decomp.) alone or mixed with glyoxal bis-2 : 4-dinitrophenylhydrazone (Found : N, 27·0%) (light absorption as above).

Bromoacetaldehyde 2 : 4-*dinitrophenylhydrazone.* (*a*) Bromoacetaldehyde (Fischer and Landsteiner, *Ber.*, 1892, **25**, 2551) on treatment with Brady's reagent gave bromoacetaldehyde 2 : 4-dinitrophenylhydrazone which separated from benzene–methanol as orange-yellow needles, m. p. 155—157° (Found : C, 32·0; H, 2·4. Calc. for $C_8H_7O_4N_4Br$: C, 31·7; H, 2·3%). Heilbron, Jones, and O'Sullivan (*J.*, 1946, 866) give m. p. 150°. Light absorption in ethanol : maxima at 2800 (ε = 11,000), 2900 (ε = 11,000), 2960 (ε = 11,500), 3050 (ε = 12,000), 3350 (ε = 11,500), and 3500 A. (ε = 11,500).

(*b*) Di-(1 : 2-dibromoethyl) ether (2·0 g.) in methanol (5 c.c.) was kept with Brady's reagent (25 c.c.) at 18° overnight. The crystals were collected and crystallised from benzene–methanol in orange-yellow needles, m. p. 155—157° (1·11 g.) alone or mixed with preparation (*a*) (Found : C, 32·2; H, 2·4%).

(*c*) Bromoacetal (0·5 g.) was kept at 18° with Brady's reagent (10 c.c.) for 2 days. The orange crystalline precipitate was filtered off (200 mg.) and extracted with hot benzene. The insoluble portion (30 mg.) crystallised from nitrobenzene–light petroleum (b. p. 100—120°) in orange needles, m. p. 320° (decomp.) alone or mixed with glyoxal bis-2 : 4-dinitrophenylhydrazone. The benzene-soluble fraction was crystallised several times from benzene–methanol, to give orange-yellow needles, m. p. 153—156° alone or mixed with bromoacetaldehyde 2 : 4-dinitrophenylhydrazone.

Reduction of di-(2 : 2-*dibromo*-1-*ethoxyethyl*) *ether.* The compound (250 mg.) was shaken with platinum [from Adams's catalyst (100 mg.)], potassium hydroxide (300 mg.), water (3 c.c.), and pure ethanol (25 c.c.) under hydrogen at 18°/1 atm. Absorption was rapid at first but ceased after 1 hour (42 c.c. Calc. for 4 mols. : 51 c.c.). The reaction mixture was filtered, acidified (Congo-red) with 2N-hydrochloric acid, and treated with an excess of a saturated solution of 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid. An immediate yellow precipitate formed which was filtered off and dried *in vacuo* (132 mg.; m. p. 130—135°). The solid was dissolved in dry benzene (20 c.c.) and adsorbed on a column of alumina (1·5 × 10 cm.), which was then washed with benzene (200 c.c.). Evaporation of the solvent gave yellow-orange crystals (90 mg.; m. p. 145—155°) which separated from benzene–light petroleum (b. p. 60—80°) as orange-yellow blades, m. p. 164—166° (75 mg., 32%) alone or mixed with acetaldehyde 2 : 4-dinitrophenylhydrazone (Found : N, 24·6. Calc. for $C_8H_8O_4N_4$: N, 25·0%). Light absorption in ethanol : maxima at 2240 (ε = 15,000), 2530 (ε = 12,000), and 3580 A. (ε = 21,500) (cf. Braude and Jones, *J.*, 1945, 498).

Bromination of paraldehyde. This was carried out substantially according to Heilbron, Jones, Julia, and Weedon (*J.*, 1949, 1823), but ultra-violet irradiation and the theoretical quantity of bromine (2 moles per mole) were used. Thus 220 g. of paraldehyde gave 650 g. of dibromoacetal, b. p. 96—103°/11 mm. The distillation residue (277 g.) solidified, and the solid (83 g.), m. p. 58—62°, was filtered off with the aid of light petroleum (b. p. 40—60°). Crystallisation from light petroleum (b. p. 60—80°) gave massive irregular prisms, m. p. 63—65°, of di-(1 : 2-dibromoethyl) ether (Found : C, 12·5; H, 1·8. Calc. for $C_4H_6OBr_4$: C, 12·3; H, 1·5%). Hibbert, Perry, and Taylor (*loc. cit.*) give m. p. 63—65°. Distillation of the oil (194 g.) obtained from the mother-liquor gave a main fraction of b. p. 100—115°/0·2 mm. (82 g.). This partly solidified; dilution with light petroleum (b. p. 40—60°) and filtration gave 30 g. of tetrabromo-ether, m. p. 61—63°.

The author thanks Professor F. S. Spring for his interest in this work and Mr. J. H. Northcote for experimental assistance.—THE ROYAL TECHNICAL COLLEGE, GLASGOW. [*Received, July 20th*, 1950.]

Nitration of Benzylidene Diacetate. By W. DAVEY and J. R. GWILT.

IN a series of preparations of *p*-nitrobenzaldehyde by Davey and Gwilt's method (*J.*, 1950, 204), it has been found that sometimes hydrolysis of benzylidene diacetate occurred, followed by immediate and vigorous oxidation to benzoic acid, whilst in other cases there was no appreciable nitration. Attempts to prevent oxidation by the addition of urea and careful temperature control effected some improvement but the reaction still proved erratic on occasions.

It has been found that the violent reaction between acetic anhydride, sulphuric acid, and benzaldehyde could be almost entirely avoided by adding a solution of benzaldehyde in acetic anhydride to a cooled mixture of acetic anhydride and sulphuric acid. This procedure enabled even commercial samples of benzaldehyde to be converted into the diacetate or nitration products.

The nitric acid nitration of benzylidene diacetate, in acetic anhydride solution at low temperatures, with and without the addition of copper nitrate has been further investigated. The nitration products were analysed by the methods suggested by Davey and Gwilt (*J. Soc. Chem. Ind.*, in the press), and it was found that the presence of copper nitrate had no appreciable effect on the reaction, which yielded about 40% of *o*-nitrobenzaldehyde and 60% of *p*-nitrobenzylidene diacetate, with 1% or less of the *m*-isomer. The small amount of the last differs from that reported by Baker and Ingold (*J.*, 1930, 431), who used somewhat similar conditions of nitration, but appears to be due to completeness of diacetate formation in the present experiments. The *o*-nitrobenzylidene diacetate, first formed, underwent hydrolysis almost quantitatively to the aldehyde, and this permitted the separation from the mixture of *p*-nitrobenzylidene diacetate, which is sparingly soluble in ethanol. Solubilities of this diester, purified by repeated crystallisation from ethanol, were as follows (in g. per 100 ml. of solution) : in methanol, 0·46 at 10°, 1·07 at 27°, and 1·88 at 37°; in ethanol, 0·16 at 10°, 0·51 at 27°, and 0·92 at 37°. While there is a slight increase in the solubility of *p*-nitrobenzylidene diacetate in the presence of impurities, particularly the isomers (cf. Bennett, *Analyst*, 1948, **73**, 191), in practice such increase has been found to be very small, enabling a separation to be readily achieved.

Experimental.—Benzaldehyde (20 g.) and acetic anhydride (40 ml.) were mixed and added slowly to a well-stirred mixture of acetic anhydride (100 ml.) and sulphuric acid (2 ml., *d* 1·84), cooled in an ice-bath. More acetic anhydride (10 ml.) was used to rinse in all the benzaldehyde. Nitric acid (40 ml.; *d* 1·52) was added, with vigorous stirring, at such a rate (over about 30 minutes) as to maintain the temperature of the mixture at 20—30°. Stirring and cooling were continued for a further 30 minutes, and the mixture was then either diluted with excess of water, or alternatively set aside for 12 hours and then diluted. The separated material was removed and extracted with ethanol at 10°; *p*-nitrobenzylidene diacetate remained, and this was hydrolysed to the aldehyde by the method described in *Org. Synth.*, Coll. Vol. II, p. 441 or by Davey and Gwilt's method (*loc. cit.*); *o*-nitrobenzaldehyde was recovered from the ethanol extract. Further quantities of these materials were obtained by ether extraction of the diluted nitration mixtures. The following results were obtained, yields being expressed as % of the benzaldehyde taken:

Hydrated copper nitrate (g.).	Hours before dilution.	Nitrobenzaldehyde.			Hydrated copper nitrate (g.).	Hours before dilution.	Nitrobenzaldehyde.		
		o.	*m.*	*p.*			*o.*	*m.*	*p.*
0	½	21	1	57	2	12	38	0·1	56
0	12	42	1	57	10	½	13	0	60
2	½	23	0·1	60	10	12	40	0	59

In some experiments, small amounts ($<5\%$) of unnitrated benzaldehyde were obtained but in no case were any oxidation products detected.

In one preliminary experiment a nitration mixture, in the absence of copper nitrate, was set aside at room temperature after the addition of the nitric acid; the temperature rose sharply after one hour, a violent reaction occurred, and *o*- and *p*-nitrobenzoic acid were obtained. For this reason, the nitration mixture was always left in an ice-bath for at least one hour after the addition of the nitric acid. By using the ethanol separation yields of 50—55% of *p*-nitro- and 25—30% of *o*-nitrobenzaldehyde have been consistently obtained.—Acton Technical College, Acton, W.3. *[Received, August* 1*st*, 1950.]

Dimorphism of Esters of scyllo*Inosose.* By S. J. Angyal and N. K. Matheson.

Posternak (*Helv. Chim. Acta*, 1941, **24**, 1046) found that penta-acetyl *scyllo*inosose existed in two forms. The higher-melting form was obtained on crystallisation from solvents containing small amounts of mineral acids, and the lower-melting from the same solvents in the absence of acids. Both forms gave the same reactions and no evidence of enolic nature was shown by either. Nevertheless, Posternak was unwilling to describe the phenomenon as dimorphism because the two forms were not produced at will by inoculation.

The same behaviour was shown by the pentabenzoate. To see whether this phenomenon was general for esters of *scyllo*inosose, the pentapropionate was prepared by us; this also crystallised in two forms, depending on the presence or absence of traces of acid.

We also failed to interconvert the two forms of the penta-acetate by inoculation. When only the merest trace of acid was present, the two forms separated unpredictably but still uninfluenced by inoculation. On evaporation of a chloroform solution, the higher-melting form was always recovered unchanged but the lower-melting gave either type of crystal indiscriminately (probably because of traces of acid in the solvent). When kept at room temperature, the lower-melting form gradually changed into the other, a process which was completed in a few days in the laboratory atmosphere but took about a month in a sealed tube.

Both forms of the acetate gave the same phenylhydrazone, and their ultra-violet absorption spectra in chloroform were identical and showed a peak (log $\varepsilon_{\text{max.}}$ 1·43 in 0·033M-solution) at 2820 A. Absorption at this wave-length is characteristic for keto-groups (Rollefson and Burton, " Photochemistry and the Mechanism of Chemical Reactions," 1939, p. 232). A very similar spectrum was reported by Posternak (*Helv. Chim. Acta*, 1946, **29**, 1994) for *scyllo*inosose itself.

Interconvertibility by inoculation is not a necessary criterion of polymorphism; other factors, such as temperature, may control the formation of the various forms. The present case seems to be an example of a dimorphism where the growth of one type of crystals is dependent on the presence of acids. Probably temporary addition of a proton to the ketonic oxygen changes the shape of the molecule and enables it to build up a different crystal lattice.

Experimental (m. p.s are corrected).—*Pentapropionyl* scyllo*inosose*. *scyllo*Inosose (2 g.) was heated on a water-bath with a mixture (19 : 1) of propionic anhydride and sulphuric acid (30 ml.) for 5 minutes and then kept for 2 hours. The mixture was cooled to 0°, and the separated crystals (4·5 g.) filtered off and washed with glacial acetic acid and ether. Recrystallisation from glacial acetic acid containing a trace of sulphuric acid gave the *propionate*, m. p. 162° (Found: C, 54·9; H, 6·5. $C_{21}H_{30}O_{11}$ requires C, 55·0; H, 6·6%). Three recrystallisations from ethanol gave the *form*, m. p. 122° (Found: C, 54·9; H, 6·5%), which was reconverted into the higher-melting form by crystallisation from glacial acetic acid with a trace of sulphuric acid.

Penta-acetyl scyllo*inosose phenylhydrazone*. To a solution of the penta-acetate (Carter *et al.*, *J. Biol. Chem.*, 1947, **174**, 423) (0·5 g.) in warm glacial acetic acid (5 ml.) phenylhydrazine (0·5 ml.) was added. After ½ hour the solution was diluted with water (25 ml.) and filtered. The solid was recrystallised from ethanol to give pale yellow needles of the *phenylhydrazone* (0·45 g.), m. p. 112—113° (Found: N, 6·0. $C_{22}H_{26}O_{10}N_2$ requires N, 5·9%). The phenylhydrazones of the low- and high-melting acetates did not depress each other's m. p.

We are indebted to the Commonwealth Science Fund for a grant which has enabled one of us (N. K. M.) to take part in this work.—Chemistry Department, University of Sydney. *[Received, August 8th*, 1950.]

An Alternative Method for the Hydrolysis of Thioamides in the Willgerodt–Kindler Reaction.

By M. A. Thorold Rogers.

The thioamides, $ArCH_2{\cdot}CS{\cdot}NRR'$, which are intermediates in the preparation of arylacetic acids by the Willgerodt–Kindler reaction (Carmack and Spielman, "Organic Reactions," 1946, Vol. III, p. 83) are usually hydrolysed by strong acid or alkali in the final stage. Occasionally (*e.g.*, Turner, *J. Amer. Chem. Soc.*, 1948, **70**, 3961; Nightingale and Carpenter, *ibid.*, 1949, **71**, 3560), the conditions required to split the thioamide link cause disruption of the remainder of the molecule. It has been found that thio-morpholides react readily with methyl iodide in acetone to give, for example, β-methylthio-β-morpholinostyrene hydriodide, $PhCH{:}C(SMe){\cdot}N{<}[CH_2]_4{>}O,HI$, which reacts readily with hot water with loss of morpholine and formation of methyl phenylthiolacetate, which can be hydrolysed to the acid under relatively mild conditions. With aqueous ammonia, the hydriodide gives phenylacetamide, and with *o*-phenylenediamine benzylbenziminazole. Under anhydrous conditions the hydriodide reacts with excess of morpholine to give ββ-dimorpholinostyrene which is sufficiently stable to be isolated but is readily hydrolysed by hot water to phenylacetmorpholide.

β-Methylthio-β-morpholinostyrene Hydriodide.—Phenylthioacetmorpholide (50 g.) was dissolved at the boiling point in dry methanol-free acetone (150 c.c.), ingress of moisture being prevented; after the temperature had fallen a few degrees, methyl iodide (25 c.c.) was added and the mixture heated under reflux for one hour. Reaction was initially vigorous, and the salt separated as white needles after a few minutes; after being cooled in ice, and filtered off, it was washed with dry benzene and dried in air. The product (69 g., 83%), m. p. 168—170°, was further purified by dissolution in dry nitromethane and addition of dry benzene, causing the separation of flat white needles, m. p. 172° (decomp.) with yellowing at above 160° (Found: C, 43·5; H, 4·65; N, 3·65. $C_{13}H_{17}ONS,HI$ requires C, 43·0; H, 4·95; N, 3·85%). The effervescence during decomposition was shown to be caused by the evolution of methyl iodide. The *hydriodide* was stable at room temperature in the dark, but became yellow in light. The base was prepared by stirring the powdered hydriodide (8·0 g.) with a cold solution of potassium hydrogen carbonate (20 g.) in water (100 c.c.) in the presence of ether (100 c.c.). After one hour only traces of solid remained, and the ether layer was separated and dried ($MgSO_4$), the solvent removed, and the *base* (4·9 g.) distilled (at about 130°/13 mm.) (Found: C, 66·45; H, 6·9. $C_{13}H_{17}ONS$ requires C, 66·4; H, 7·25%). The clear yellow distillate was soluble in dilute hydrochloric acid, and the solution decomposed on warming, as did the hydriodide in water (see below).

Action of Water on the Methylthio-hydriodide.—The hydriodide (2·7 g.) was dissolved in water (150 c.c.) with gentle warming; a clear solution was obtained, but this clouded almost at once and the resultant oil was steam-distilled and extracted with ether from the distillate. Slow evaporation of the ether left methyl phenylthiolacetate (0·98 g., 61·5%) (Found: C, 64·7; H, 6·1. Calc. for $C_9H_{10}OS$: C, 65·05; H, 6·05%). The thio-ester was further characterised by being heated under reflux with 2N-sodium hydroxide in a slow stream of nitrogen. The issuing gases gave (i) a crystalline precipitate of mercuric thiomethoxide (m. p. 170°) with mercuric cyanide; (ii) a red colour with sodium nitroprusside; (iii) a green colour with isatin in strong sulphuric acid.

The hydriodide was refluxed with ammonia solution (*d* 0·88) for 0·5 hour. Methanethiol was evolved, and from the residue there was obtained phenylacetamide, m. p. 154°. With *o*-phenylenediamine (4·2 g., 2 mols.), the hydriodide (5·2 g.) in dry nitromethane (25 c.c.) gave, after 3 hours' refluxing and cooling, 2-benzylbenziminazole (3·9 g.), m. p. 181—183°.

ββ-Dimorpholinostyrene.—The hydriodide (23 g.) and dry morpholine (15 c.c.) were warmed on the steam-bath with exclusion of moisture for 2 hours. Methanethiol was liberated, and the solid passed into solution. After cooling, the crystalline residue was mixed to a paste with ice-water, filtered off, and rapidly dried (P_2O_5) in a vacuum; the product (11·8 g., 71·5%) had m. p. 125—129°. Crystallisation from *cyclo*hexane gave white plates of the *dimorpholinostyrene* (7·7 g.; m. p. 130—132°), which on recrystallisation from dry benzene had m. p. 131—132° (Found: C, 70·4; H, 8·1; N, 10·3. $C_{16}H_{22}O_2N_2$ requires C, 70·05; H, 8·05; N, 10·25%). The *picrate*, made in nitromethane solution, and precipitated by the addition of dry ether, formed canary-yellow needles (from acetonitrile–ether), m. p. 160° (Found: C, 52·65; H, 4·95; N, 14·3. $C_{16}H_{22}O_2N_2,C_6H_3O_7N_3$ requires C, 52·5; H, 4·95; N, 13·9%). A methiodide, m. p. 168—170° (decomp. not sharp), separated when the base and methyl iodide were mixed in benzene. It was deliquescent, and darkened in light.

Action of Water on ββ-Dimorpholinostyrene.—The base (1·6 g.) and water (20 c.c.) were heated under reflux for 5 minutes; the alkaline solution was acidified (HCl) and extracted with chloroform, from which was obtained *phenylacetmorpholide*, m. p. 67—68°, not depressed by a sample made through the acid chloride (Found: C, 70·35; H, 6·8. $C_{12}H_{15}O_2N$ requires C, 70·25; H, 7·3%). Moist air slowly caused the same hydrolysis.—Imperial Chemical Industries Ltd., Research Laboratories, Hexagon House, Blackley, Manchester, 9. [*Received, August* 11*th*, 1950.]

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p-*Bromophenacyl Formate.* By John Frederick Grove and P. J. Suter.

The formation of phenacyl esters is now widely used for the characterisation and identification of carboxylic acids, and the conditions for their preparation have been carefully studied by Reid and his collaborators (Rather and Reid, *J. Amer. Chem. Soc.*, 1919, **41**, 75). Judefind and Reid (*ibid.*, 1920, **42**, 1043) stated that sodium formate did not react with *p*-bromophenacyl bromide, the reagent being recovered unchanged. Subsequently, Moses and Reid (*ibid.*, 1932, **54**, 2101) recorded the melting point of *p*-bromophenacyl formate as 135·2° (decomp.) and Hurd and Christ (*ibid.*, 1935, **57**, 2005) independently gave a detailed preparation, in which sodium formate and *p*-bromophenacyl bromide were heated under reflux in 60—70% ethanol; they reported the melting point of the derivative to be 140°.

When the preparation of *p*-bromophenacyl formate, as described by Hurd and Christ, was attempted, a substance, m. p. 138—140° (decomp.), was obtained, but rather surprisingly, the infra-red spectrum showed only one band in the C=O region at 1685 cm.$^{-1}$, the band expected for formate C=O at 1730 cm.$^{-1}$ being absent. Analysis and a mixed melting-point determination revealed that the substance was, in fact, *p*-bromophenacyl alcohol.

When, however, formic acid was almost neutralised with 0·1N-sodium ethoxide, as recommended by Moses and Reid (*loc. cit.*), and the solution then heated under reflux with one equivalent of *p*-bromophenacyl bromide in 95% ethanol, the product melted indefinitely between 90° and 99°, the melting point being depressed by admixture of the product with *p*-bromophenacyl bromide. The crude product could not be separated satisfactorily into its components by fractional crystallisation from ethanol but chromatography of a benzene solution on activated alumina yielded two substances *A* and *B*.

Substance *A*, m. p. 99°, gave a correct analysis for *p*-bromophenacyl formate. The infra-red spectrum showed bands in the double-bond stretching region at 1725 and 1692 cm.$^{-1}$ due to ester and alkyl aryl ketone C=O, respectively.

Substance *B*, m. p. 136—139° (decomp.), was *p*-bromophenacyl alcohol.

Hydrolysis of the ester, m. p. 99°, in the presence of barium carbonate yielded *p*-bromophenacyl alcohol, and formic acid, identified after reduction to formaldehyde by the chromotropic acid test. The ester was recovered unchanged after one hour's refluxing with 70% ethanol, but was hydrolysed quantitatively in the presence of 3 mols. of sodium formate. The failure of the method described by Hurd and Christ may, therefore, be attributed to the large excess of sodium formate used.

Experimental.—***Hurd and Christ's procedure.*** Sodium formate (1 g.) in water (5 c.c.) was added to *p*-bromophenacyl bromide (1 g.) in boiling ethanol (10 c.c.), and the mixture heated under reflux for one hour. The product crystallised from aqueous ethanol in colourless plates or long needles, m. p. 138—140° (decomp.) not depressed on admixture with an authentic specimen of *p*-bromophenacyl alcohol (Found : C, 44·8, 44·5; H, 3·2, 3·4; Br, 38·6. Calc. for $C_8H_7O_2Br$: C, 44·7; H, 3·3; Br, 37·2%).

p-***Bromophenacyl formate.*** Formic acid (0·47 g.) was neutralised with 0·1N-sodium ethoxide, and the solution made just acid by the addition of a trace of formic acid. *p*-Bromophenacyl bromide (2·84 g.) in ethanol (30 c.c.) was added, and the mixture heated under reflux for one hour. The product obtained on concentration of the solvent was dissolved in ether and washed with water. Evaporation of the ether left a crystalline product, m. p. 89—99° (0·6 g.), which on recrystallisation from ethanol gave colourless plates (0·3 g.), melting partially at 89—91° but not completely melted at 110°. The recrystallised product was dissolved in benzene and filtered through a column of activated alumina (9 g.) of pH 6, 10-c.c. fractions being collected and examined separately.

The solid contents (0·1 g.) of fractions 1—5 were combined and crystallised twice from ethanol giving substance *A*, as colourless plates, m. p. 99° depressed by admixture with *p*-bromophenacyl bromide and with *p*-bromophenacyl alcohol [Found: C, 44·7, 44·8; H, 2·9, 2·9; Br, 33·3%; *M* (Rast), 214. $C_9H_7O_3Br$ requires C, 44·4; H, 2·9; Br, 32·9%; *M*, 243].

Fractions 6—7 were combined (0·03 g.) and crystallised from ethanol giving substance *B*, as colourless plates, m. p. 136—139° (decomp.) not depressed by *p*-bromophenacyl alcohol.

We are indebted to Mr. H. A. Willis, Imperial Chemical Industries Limited, Plastics Division, for the use of infra-red facilities. Microanalyses were carried out by Drs. Weiler and Strauss, Oxford.—
IMPERIAL CHEMICAL INDUSTRIES LIMITED, BUTTERWICK RESEARCH LABORATORIES, THE FRYTHE, WELWYN, HERTS. [*Received, September* 1*st*, 1950.]