## 246. *The Preparation and Identification of the Double Salts* $AgBr,2TlBr$, $AgI,2TlI$, *and* $AgI,TlI$.

By H. Hirsch.

Dombrovskaya,[1] studying the phase diagram of the systems $Tl_2SO_4$–$2AgBr$–$2TlBr$ and $Tl_2SO_4$–$2AgBr$–$Ag_2SO_4$, obtained evidence for the existence of the compound $AgBr,2TlBr$. This was the only reference to a double salt of silver bromide and thallium bromide which could be found before the present work was begun.

Berg and Lepeshkov,[2] studying the reciprocal salt system $AgNO_3 + TlI = AgI + TlNO_3$ in the molten state, found evidence for the existence of the compounds $AgI,2TlI$ and $AgI,TlI$. Platonov,[3] studying the system AgI–TlI, found evidence for the compound $AgI,2TlI$ only.

As regards other double halides of two univalent metals, Brink and MacGillavry [4] have reported the preparation and structure of $K_2CuCl_3$, $Cs_2AgCl_3$, and $Cs_2AgI_3$, and Lyalikov [5] the preparation of $Cs_2AgBr_3$, $CsAgBr_2$, and $(NH_4)_2AgBr_3$.

In order to determine whether double salts of silver and thallous bromide, and of silver and thallous iodide, are formed by crystallisation from solution, co-precipitates were prepared and examined by *X*-ray diffraction. Our results indicate existence of the double salts formulated in the title, and no others in these systems.

*Experimental.*—Solutions of thallous nitrate and silver nitrate were added successively to solutions containing an excess of either potassium bromide or iodide and 1% of gelatin at 60°. The gelatin acted as a protective colloid, keeping the precipitate in a dispersed state and thus facilitating rapid attainment of equilibrium. The relative amounts of thallous and silver nitrate were varied and the co-precipitates were allowed to reach equilibrium at the precipitation temperature during 1 hr. After centrifugation and washing of the precipitates, *X*-ray diffraction patterns were recorded, with a crystal focusing monochromator camera and copper-$K_\alpha$ radiation. The relative diffraction line intensities at the film plane were measured from microdensitometer tracings of several patterns at density levels for which direct proportionality between density and intensity is obtained.

*Results.*—Co-precipitates of thallous and silver bromide formed a pure double salt when the atomic ratio Tl : Ag used was slightly greater than 2 : 1. At other compositions the double salt contained an excess of either thallous (Tl : Ag $\gg$ 2 : 1) or silver bromide (Tl : Ag $<$ 2 : 1). indicating that only one double salt is formed and that its composition is $AgBr,2TlBr$, Chemical analysis of a preparation whose diffraction pattern indicated reasonable purity gave Ag, 14·7; Br, 31·1% (Calc. for $AgBr,2TlBr$: Ag, 14·25; I, 31·7%). That the molar ratio of Tl : Ag necessary to give the pure double salt is slightly greater than 2 : 1 is probably due to the greater solubility of thallous bromide. It was indeed found that prolonged washing completely converted the double salt into silver bromide as a result of preferential solution of thallous bromide. In co-precipitates of thallous iodide and silver iodide two double salts were identified, both by their colours and by their *X*-ray diffraction patterns. When the molar ratio Tl : Ag was 2 : 1 a white precipitate of a salt $AgI,2TlI$ was obtained (Found: Ag, 12·0; I, 42·3. Calc.: Ag, 12·0; I, 42·4%). When the molar ratio of Tl : Ag was 1 : 1, a deep yellow precipitate of a salt $AgI,TlI$ was obtained (Found: Ag, 18·8; I, 44·8. Calc.: Ag, 19·0; I, 44·8%).

The *X*-ray diffraction patterns and colours of the co-precipitates indicate that $AgI,2TlI$ is the equilibrium phase in presence of an excess of thallous iodide, and that $AgI,TlI$ is the

[1] Dombrovskaya, *J. Gen. Chem.* (*U.S.S.R.*), 1933, **3**, 291; *Chem. Abs.*, 1934, **28**, 2250.
[2] Berg and Lepeshkov, *Izvest. Sekt. fiz.-khim. Anal., Inst. obshchei neorg. Khim.*, 1947, **15**, 144; *Chem. Abs.*, 1950, **44**, 7134.
[3] Platonov, *Trudy Moskov. Sel'sko-Khoz. Akad im. K.A. Timiryazeva*, 1946, No. 36, 13; *Chem. Abs.*, 1950, **44**, 9236.
[4] Brink and MacGillavry, *Acta Cryst.*, 1949, **2**, 158.
[5] Lyalikov, *Doklady Akad. Nauk S.S.S.R.*, 1949, **65**, 171; *Chem. Abs.*, 1949, **43**, 4971.

equilibrium phase in presence of an excess of silver iodide. Compositions intermediate between those of the double salts give rise to mixtures of the two.

Values of $\sin^2\theta$ and the relative line intensities of the first twelve diffraction lines of the three double salts are given in the Table. The first thirty-seven lines of the diffraction pattern of the double salt AgI,TlI could be indexed on the basis of a tetragonal unit cell with parameters $a = b = 8{\cdot}34$, $c = 7{\cdot}66$ Å.

The chemical analyses were carried out by C. B. Dennis of these Laboratories.

The diffraction patterns of the compounds.

| | AgBr,2TlBr | | AgI,2TlI | | AgI,TlI | |
|---|---|---|---|---|---|---|
| Line no. | Relative intensity | $\sin^2\theta$ | Relative intensity | $\sin^2\theta$ | Relative intensity | $\sin^2\theta$ |
| 1 | 24 | 0·0340 | 10 | 0·0307 | 11 | 0·0343 |
| 2 | 46 | 0·0389 | 20 | 0·0353 | 46 | 0·0529 |
| 3 | 22 | 0·0583 | 4 | 0·0450 | 11 | 0·0576 |
| 4 | 68 | 0·0632 | 11 | 0·0527 | 40 | 0·0683 |
| 5 | 97 | 0·0729 | 34 | 0·0539 | 100 | 0·0745 |
| 6 | 100 | 0·0827 | 100 | 0·0568 | 15 | 0·0855 |
| 7 | 7 | 0·0875 | 88 | 0·0655 | 8 | 0·1088 |
| 8 | 3 | 0·0978 | 99 | 0·0750 | 1 | 0·1210 |
| 9 | 6 | 0·1071 | 99 | 0·0756 | 13 | 0·1339 |
| 10 | 19 | 0·1120 | 6 | 0·0808 | 5 | 0·1365 |
| 11 | 15 | 0·1314 | 5 | 0·0885 | <1 | 0·1538 |
| 12 | 7 | 0·1362 | 6 | 0·0962 | 16 | 0·1551 |

RESEARCH LABORATORIES, KODAK LIMITED,
WEALDSTONE, HARROW, MIDDLESEX.

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## 247. *The Synthesis and Reactions of Branched-chain Hydrocarbons. Part XVI.* Bromination in the Liquid Phase by* N-*Bromosuccinimide.*

By J. R. B. BOOCOCK and W. J. HICKINBOTTOM.

*N*-BROMO-AMIDES and -imides have a wide application for the bromination of CH groups activated by an adjacent double bond [1] (allylic substitution) or by an aryl group.[2] They have also been used successfully for the bromination of phenols,[3,4] thiophens,[3] and furans.[5] The only reported applications to saturated hydrocarbons are the reaction of *N*-bromosuccinimide with cyclohexane [6] and decalin; [7] Wohl [8] has reported its reaction with n-butyl bromide.

In this paper it is shown the *N*-bromosuccinimide can be used to brominate alkanes if benzoyl peroxide is present. The yields are relatively low and the bromination is accompanied by the evolution of hydrogen bromide, although, in the light of later studies it is probable that the yield of bromo-compounds could be improved by careful adjustment of such factors as temperature of reaction and the concentration of benzoyl peroxide.

* Part XV, *J.*, 1963, 230.

[1] Ziegler, Späth, Schaaf, Schumann, and Winkelmann, *Annalen*, 1942, **551**, 80.
[2] Bredt and Hof, *Ber.*, 1900, **33**, 21; Karrer and Schmid, *Helv. Chim. Acta*, 1946, **29**, 573; Buu-Hoï, *Annalen*, 1944, **556**, 1.
[3] Steinkopf and Otto, *Annalen*, 1920, **424**, 61.
[4] Wohl and Jaschinowski, *Ber.*, 1921, **54**, 476.
[5] Buu-Hoï, *Compt. rend.*, 1946, **222**, 1441; 1947, **224**, 658; Runde, Scott, and Johnson, *J. Amer. Chem. Soc.*, 1930, **52**, 1284.
[6] Barnes, *J. Amer. Chem. Soc.*, 1948, **70**, 145.
[7] Ford and Waters, *J.*, 1952, 2240.
[8] Wohl, *Ber.*, 1919, **52**, 51.

For the bromination of the isoalkanes it has been established that olefins are present in the products. It is the occurrence of such side reactions that makes this method unsuitable as a quantitative method of determining the rate of bromination.

*Experimental.*—The hydrocarbons were purified as described in a previous paper.[9] Bromination was carried out by the following general method.

*N*-Bromosuccinimide (17 g., 0·096 mole), benzoyl peroxide (1·8 g., 0·0074 mole), and the hydrocarbon (50 g.) were maintained together at 90° under a condenser. The mixture was stirred until there was no further bromination, then cooled and poured into light petroleum (250 c.c., b. p. <40°). The precipitate of succinimide was collected, the filtrate freed from the excess of solvent, and the residue of bromoalkanes distilled.

(*a*) *n-Heptane.* A mixture of bromoheptanes (6 g.) obtained after 14 hr. had b. p. 59—61°/18 mm., $n_D^{20}$ 1·4507 (Found: C, 48·0; H, 8·6; Br, 43·2. Calc. for $C_7H_{15}Br$: C, 46·9; H, 8·4; Br, 44·7%).

(*b*) *Dodecane.* The product obtained after 28 hr. was mainly bromododecanes, b. p. 94—102°/10 mm., $n_D^{20}$ 1·4580 (4·0 g.) (Found: C, 58·0; H, 10·1; Br, 32·0. Calc. for $C_{12}H_{25}Br$: C, 57·8; H, 10·1; Br, 32·1%); there was a fraction (0·9 g.), b. p. 102—110°/1·0 mm., $n_D^{20}$ 1·4630, containing dibromododecanes (Found: Br, 35·5%).

(*c*) *Octadecane.* In this bromination a smaller amount of benzoyl peroxide (0·05 g.) was used and the reaction required 50 hr. for completion. The greater part of unchanged octadecane was removed by chromatography on silica gel with light petroleum (b. p. 80—100°). A yellow liquid (5·5 g.) was obtained (Found: C, 75·1; H, 13·2; Br, 11·6. Calc. for $C_{18}H_{37}Br$: C, 64·8; H, 11·2; Br 24·0%), which contained bromo-octadecanes.

(*d*) 2,2,4-*Trimethylpentane.* After 10 hr. bromo-2,2,4-trimethylpentanes (6·8 g.), b. p. 56—60°/14 mm., $n_D^{20}$ 1·4596—1·4618 (Found: C, 50·3; H, 9·1; Br, 40·9. Calc. for $C_8H_{17}Br$: C, 49·7; H, 8·9; Br, 41·4%), were obtained. The recovered 2,2,4-trimethylpentane contained some olefin.

(*e*) 2,3,4-*Trimethylpentane.* Even when a trace of benzoyl peroxide was used as promoter, there was extensive dehydrobromination if the reaction was allowed to go to completion. If the reaction was stopped after 15 min. a small amount of bromo-compound was obtained (0·7 g.; b. p. 40—60°/15 mm.) (Found: C, 49·9; H, 8·5; Br, 41·4%). The recovered alkane contained some olefin.

(*f*) *Methylcyclohexane.* The reaction was stopped after 3 hr. because of the vigorous evolution of hydrogen bromide. The product contained unsaturated material and a small amount of bromocyclohexanes (1·8 g.), b. p. 62—66°/16 mm., $n_D^{20}$ 1·4987 (Found: C, 48·6; H, 7·1; Br, 44·4. Calc. for $C_7H_{13}Br$: C, 47·5; H, 7·4; Br, 45·1%).

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CHEMISTRY DEPARTMENT, QUEEN MARY COLLEGE,
MILE END ROAD, LONDON, E.1. [*Received, February 20th,* 1962.]

[9] Boocock and Hickinbottom, *J.*, 1963, 230.

## 248. *The Preparation of Neopentyl- and t-Butyl-oxiran.*

By S. J. Hurst and J. Malcolm Bruce.

Passage of chlorine into a solution of 4,4-dimethylpent-1-ene in aqueous pyridine sulphate [1] afforded a mixture of 1-chloro-4,4-dimethylpentan-2-ol and 2-chloro-4,4-dimethylpentan-1-ol, from which neopentyloxiran was obtained by treatment with potassium hydroxide. Application of a similar procedure to 3,3-dimethylbut-1-ene gave a complex mixture. The structure of neopentyloxiran was established by periodate cleavage of the derived glycol, which afforded 3,3-dimethylbutanal and formaldehyde.

Reduction [2] of 1-bromo-3,3-dimethylbutan-2-one with sodium borohydride yielded the corresponding bromo-alcohol, which with potassium hydroxide afforded t-butyloxiran. This route is more convenient than that [3] starting with chloroacetaldehyde.

The structures of the oxirans are supported by their infrared [4,5] and mass spectra. In common with those of other ethers,[6] the parent mass peaks are of low intensity.

*Experimental.*—Solvents were purified by fractional distillation and were removed from solutions on the water-bath, where necessary under reduced pressure. Solutions were dried with sodium sulphate. Infrared spectra (absorption is strong unless stated otherwise) were determined as liquid films with Perkin-Elmer model 21 and Unicam model S.P. 200 double-beam spectrometers. Mass spectra were determined with a Metropolitan-Vickers model MS2 spectrometer; unless stated otherwise, only strong mass peaks are listed. M. p.s are corrected. The oxirans were distilled, with a variable take-off head, through a 170 × 16 mm. column packed with 4-mm. glass Fenske helices.

*Neopentyloxiran.* Chlorine (2—3 l./hr.) was passed for 4½ hr. through a vigorously stirred mixture of 4,4-dimethylpent-1-ene [7] (37 c.c., 25·3 g.), water (1·1 l.), pyridine (660 c.c.), and aqueous 60% sulphuric acid (0·5 c.c.) at 10—11°, and stirring at this temperature was then continued for a further 30 min. The mixture was treated with aqueous 10% hydrochloric acid (1·2 l.) and extracted with pentane, and the extract was washed successively with aqueous 7% hydrochloric acid, aqueous 10% sodium hydrogen carbonate, and water, and dried. Removal of the solvent and distillation of the residue gave a mixture of chloro-alcohols (23·1 g., 59%), b. p. 75—90°/18·5 mm., $n_D^{25}$ 1·4483, $\nu_{max.}$ 3397 broad, 1086 (CH–OH [8]), 1063 ($CH_2$–OH [8]) cm.$^{-1}$, which slowly evolved hydrogen chloride (Found: C, 56·3; H, 9·5. Calc. for $C_7H_{15}ClO$: C, 55·8; H, 9·4%). This material (17·6 c.c., 17·2 g.) was added (1 drop/sec.) to a mixture of potassium hydroxide (100 g.) and water (12 c.c.) at 180—200°, and the distillate, in pentane, was washed with water and then dried. Removal of the solvent and distillation of the residue gave the *oxiran* (8·7 g., 67%), b. p. 126—128°/744 mm., $n_D^{24}$ 1·4089, $\nu_{max.}$ 3051, 1265, 1031w, 901, 828, 742m cm.$^{-1}$ (cf. refs. 4, 5), mass spectrum 114w, 57, 53, 43, 41, 39, 29, 27, 26 (Found: C, 73·9; H, 11·8. $C_7H_{14}O$ requires C, 73·6; H, 12·3%). Vapour-phase chromatography indicated a purity of ⩽99%.

*4,4-Dimethylpentane-1,2-diol.* A mixture of the foregoing oxiran (500 mg.), dioxan (2 c.c.), and aqueous 2% potassium hydroxide (5 c.c.) was refluxed for 24 hr., cooled, and diluted with water (3 c.c.). The mixture was extracted with ether, and the extract was washed with water and dried. Removal of the solvent, and distillation [bulb-to-bulb, 95° (bath)/1 mm.] of the residue afforded the *diol* (445 mg., 77%) as a hygroscopic oil, $\nu_{max.}$ 3340 broad, 1084 (CH–OH [8]), 1040 ($CH_2$–OH [8]) cm.$^{-1}$ (Found: C, 63·4; H, 11·8. $C_7H_{16}O_2$ requires C, 63·6; H, 12·2%). The *di-p-nitrobenzoate*, very pale yellow needles (from ethanol), had m. p. 146·5° (Found: C, 58·4; H, 4·9; N, 6·6. $C_{21}H_{22}N_2O_8$ requires C, 58·6; H, 5·2; N, 6·5%).

[1] Cf. Guyer, Bieler, and Pedrazzetti, *Helv. Chim. Acta*, 1956, **39**, 423.
[2] Cf. Goto and Kishi, *Tetrahedron Letters*, 1961, 513; Fuchs, *J. Amer. Chem. Soc.*, 1956, **78**, 5612.
[3] E. Gryszkiewicz-Trochimowski and O. Gryszkiewicz-Trochimowski, *Bull. Soc. chim. France*, 1953, 125.
[4] Tobin, *Spectrochim. Acta*, 1960, **16**, 1108; Henbest, Meakins, Nicholls, and Taylor, *J.*, 1957, 1459.
[5] Jones and Sandorfy, in Weissberger (ed.), "Technique of Organic Chemistry," Interscience Publ., Inc., New York, 1956, Vol. IX, p. 440.
[6] Beynon, "Mass Spectrometry and its Applications to Organic Chemistry," Elsevier Publ. Co., Amsterdam, 1960, p. 362.
[7] Whitmore and Homeyer, *J. Amer. Chem. Soc.*, 1933, **55**, 4555.
[8] Ref. 5, p. 432.

*Cleavage of 4,4-dimethylpentane-1,2-diol.* Periodic acid (1·2 c.c., 50% w/w aqueous $HIO_4,2H_2O$) in water (10 c.c.) was added all at once to a solution of the diol (335 mg.) in aqueous 30% methanol (15 c.c.) at 23°, and the mixture was maintained at this temperature, with occasional shaking, for 2 hr., then extracted with pentane. The extract was washed with water, then dried, and the solvent was cautiously removed, leaving 3,3-dimethylbutanal (250 mg., 98%) as a mobile liquid, $\nu_{max.}$ 1715 cm.$^{-1}$, which afforded a dimedone derivative, plates (from aqueous methanol), m. p. 168·5—169° (lit.,[7] 167°), and a 2,4-dinitrophenylhydrazone, orange needles (from methanol), m. p. 146° (lit.,[7] 146—147°). Distillation of the aqueous phase from the pentane extraction, and treatment of the distillate with dimedone afforded the dimedone derivative of formaldehyde (445 mg., 60% based on diol), m. p. and mixed m. p. 190°.

*1-Bromo-3,3-dimethylbutan-2-ol.* Sodium borohydride (9·7 g.) in distilled water (120 c.c.) was added during 1 hr. to a stirred solution of 1-bromo-3,3-dimethylbutan-2-one [9] (80 g.) in distilled water (120 c.c.), dioxan (345 c.c.), and methanol (385 c.c.). The temperature rose to 38°. Stirring was continued for 3 hr., and the mixture was then treated with aqueous 2% sulphuric acid (2·3 l.), and sodium chloride (250 g.) and extracted with ether. The extracts were washed with aqueous 25% sodium chloride, dried, and the solvent was removed. Distillation of the residue afforded the *bromo-alcohol* (43·5 g., 54%), b. p. 45—46°/4 mm., $n_D^{23}$ 1·4683, $\nu_{max.}$ 3462 broad, 1082 (CH–OH [8]) cm.$^{-1}$ (Found: C, 40·2; H, 7·2; Br, 42·7. $C_6H_{13}BrO$ requires C, 39·8; H, 7·2; Br, 44·1%).

*t-Butyloxiran.* The foregoing bromo-alcohol (25 g.) was added (1 drop/sec.) to a mixture of potassium hydroxide (80 g.) and water (10 c.c.) at 140—160°, and the distillate was dried and distilled, to give the oxiran (9·4 g., 68%), b. p. 97°/763 mm., $n_D^{22}$ 1·3993 (lit.,[3] b. p. 86°/760 mm., $n_D^{25}$ 1·3977), $\nu_{max.}$ 3075, 1252, 1048m, 1020w, 916, 848 cm.$^{-1}$ (cf. refs. 4, 5), mass spectrum 100w, 85, 70, 57, 43, 42, 41, 39, 29, 27 (Found: C, 72·1; H, 12·3. Calc. for $C_6H_{12}O$: C, 71·9; H, 12·1%). Vapour-phase chromatography indicated a purity of $\geq$99%. When heated (sealed tube) at 140—180° for 7 hr. with aqueous 2% potassium hydroxide (5 c.c.), the oxiran (3 c.c.) afforded 3,3-dimethylbutane-1,2-diol, m. p. 45—46° (lit.,[3] 45—46°), $\nu_{max.}$ 3380 broad, 1090 (CH–OH [8]), 1044 ($CH_2$–OH [8]) cm.$^{-1}$, the di-*p*-nitrobenzoate of which crystallised from ethanol as very pale yellow needles, m. p. 143—143·5° (lit.,[3] 140·5—141°) (Found: C, 57·8; H, 5·0; N, 6·7. Calc. for $C_{20}H_{20}N_2O_8$: C, 57·7; H, 4·8; N, 6·7%).

We thank Dr. J. H. Baxendale for the measurement of mass spectra, and the University of Manchester, and Courtaulds Ltd. for the award of Research Studentships to one of us (S. J. H.).

Department of Chemistry, University of Manchester. [*Received, July 18th,* 1962.]

[9] Jackman, Klenk, Fishburn, Tullar, and Archer, *J. Amer. Chem. Soc.*, 1948, **70**, 2884.

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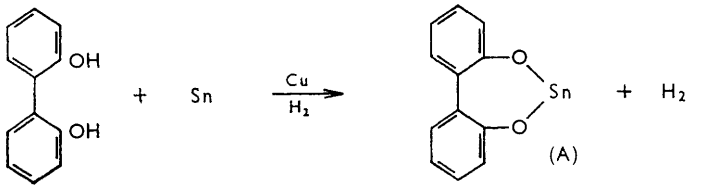
## 249. *The Reaction of Tin with Dihydric Phenols: The Direct Synthesis of Tin*(II) *Heterocycles.*

By J. J. Zuckerman.

The direct synthesis of organotin halides has been studied by Rochow *et al.*,[1] but no information is available on the reactivity of alcohols and phenols with tin. Silicon is known to react with dihydric phenols to give cyclic spiro-esters in good yield,[2] and this Note describes a similar study of the action of catechol and 2,2′-dihydroxybiphenyl on a tin–copper contact mass. The reaction with catechol at 150° under a high pressure of hydrogen gives a solid from which *o*-phenylenedioxytin(II) was isolated by sublimation. 2,2′-Dihydroxybiphenyl gives 2,2′-biphenylylenedioxytin(II) (A) under similar conditions.

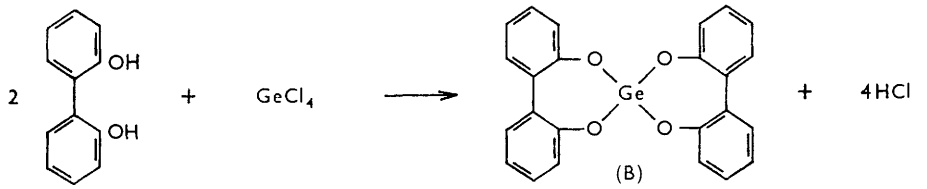
[1] Rochow and Smith, *J. Amer. Chem. Soc.*, 1953, **75**, 4103, 4105.
[2] Zuckerman, *J.*, 1962, 873.

These compounds are notable for their high thermal stability (*e.g.*, in air to ~500°). They are insoluble in all common solvents, but have a small solubility in donating solvents such as warm pyridine, from which they can be recovered unchanged. This precluded molecular-weight determination, and the low volatility indicates some degree of polymerization.




(A)

The formation of tin(II) rather than of tin(IV) derivatives is of interest since, although such tin(II) compounds have been observed in the direct synthesis of organotin halides, they are normally alkylated and halogenated in the course of reaction.[1] Also, reaction of




(B)

germanium tetrachloride with 2,2′-dihydroxybiphenyl gives bis-2,2′-biphenylylenedioxygermanium (B). Reaction of a germanium–copper contact mass with catechol and 2,2′-dihydroxybiphenyl failed to give germanium esters. Reaction of silicon with the two phenols gives the expected silicon(IV) derivative in each case.[2] Tin(IV) alkoxides are known,[3] but they are of low hydrolytic and thermal stability. All the cyclic esters reported above hydrolyze in alcoholic potassium hydroxide to regenerate the organic starting material.

A stable grey solid was obtained by reaction of catechol with lead–copper. The infrared spectrum of this material resembled that of *o*-phenylenedioxytin(II), but only lead oxide and benzene were recovered on sublimation *in vacuo* above 500°. Hydrolysis liberated catechol.

*Experimental.*—Contact masses were prepared by mixing the finely divided element with copper powder (10% by wt.). A gift of germanium from Dr. C. Gordon Peattie, Texas Instruments, Inc., is gratefully acknowledged.

*Analyses.* Carbon and hydrogen were determined by the Microanalytical Department of this Laboratory. A gravimetric method for silicon [2] was applied to the determination of germanium and tin, except that the oxides were not treated with hydrofluoric acid. High results were obtained on samples of stannic oxide ignited for an insufficient length of time. Ignition for *ca.* 2 hr. gave residues of white oxide which exhibited little weight gain in air.

*Reaction with tin.* (*a*) Catechol (2 mol.) was heated at 150° with a tin–copper contact mass (0·1 atom-equiv. of tin) under hydrogen at 128 atm. for 7·5 hr. The grey solid product was sublimed to recover starting material, and then heated at 300° *in vacuo* to give *o-phenylenedioxytin*(II) as a white powder (Found: C, 31·9; H, 2·0; Sn, 52·3. $C_6H_4O_2Sn$ requires C, 31·75; H, 1·8; Sn, 52·3%) which did not melt at 500°, although there was some decomposition in air at this temperature. The product was insoluble in common organic solvents, but was slightly soluble in warm pyridine, dimethylformamide, and tetrahydrofuran, and could be recovered from these solvents unchanged. The material was apparently stable towards hydrolysis, but treatment with alcoholic potassium hydroxide regenerated catechol.

[3] Maire, *Ann. Chim.* (*France*), 1961, **6**, 969.

(*b*) 2,2′-Dihydroxybiphenyl (0·25 mole) was heated at 280° with a tin–copper contact mass (0·5 mole of tin) under hydrogen at 100 atm. for 5·5 hr. Starting material was recovered and sublimation *in vacuo* at 340° gave *2,2′-biphenylylenedioxytin*(II) (Found: C, 47·2; H, 2·7; Sn, 39·3. $C_{12}H_8O_2Sn$ requires C, 47·5; H, 2·6; Sn, 39·3%) as a white powder which did not melt at 500°, although there was some decomposition in air at this temperature. The material was not particularly prone to hydrolysis, but 2,2′-dihydroxybiphenyl was recovered after storage in moist air for long periods. The product did not dissolve in organic solvents, but was slightly soluble in warm pyridine, dimethylformamide, and tetrahydrofuran, and could be recovered unchanged from these solvents.

*Reaction with lead.* The tarry product from the action of catechol on a lead–copper contact mass at 284° under hydrogen at 84 atm. for 5 hr. gave some benzene and a phenolic liquid on distillation *in vacuo*. Sublimation *in vacuo* above 500° yielded benzene and an off-white powder which in concentrated hydrochloric acid liberated chlorine. Its *X*-ray powder photograph was identical with that of a sample of lead oxide. The grey solid product was insoluble in organic solvents and did not melt at 500°, but was hydrolyzed to catechol. The infrared spectrum of this material (contaminated with lead) contained no hydroxyl bands, and in general resembled that of the product of catechol with tin metal. Analysis confirmed the presence of carbon and hydrogen (Found: C, 9·1; H, 1·3%).

*Reaction with chlorogermanes.* Germanium tetrachloride [4] reacted with catechol in boiling sodium-dried ether under nitrogen, to liberate hydrogen chloride for 5 hr. and produce a reddish solution. Sublimation pyrolyzed the product. The white glassy material obtained on reaction of catechol with a germanium–copper contact mass behaved similarly. 2,2′-Dihydroxybiphenyl was pyrolyzed when heated with germanium–copper, but reacted (0·07 mole) with germanium tetrachloride (0·035 mole) in ether to give a white solid, m. p. 340° (after sublimation *in vacuo* at 240°). This material gave a negative test for chloride with silver nitrate and was only slightly soluble in organic solvents. Hydrolysis regenerated 2,2′-dihydroxybiphenyl. The product appeared to be *bis-2,2′-biphenylylenedioxygermanium* (Found: C, 64·3; H, 4·05; Ge, 16·8. $C_{24}H_{16}O_4Ge$ requires C, 65·4; H, 3·7; Ge, 16·5%). Rast molecular-weight determinations showed the compound to be monomeric (Found: *M*, 428. Required: *M*, 440).

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UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, July 19th*, 1962.]

[4] Dennis and Hance, *J. Amer. Chem. Soc.*, 1922, **44**, 299.

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## 250. *The Preparation and Properties of Diethyl Methylthiomethylphosphonate.*

By M. GREEN.

It is known [1] that phosphonates containing an electron-withdrawing group can form stabilised carbanions which react with carbonyl compounds to yield an olefin and a phosphate salt, thus:

$$\underset{\text{(I)}}{(RO)_2PO{\cdot}CH_2X} + NaH \longrightarrow H_2 + (RO)_2PO{\cdot}CHX^-Na^+ \xrightarrow[R_2CO]{} (RO)_2PO_2Na + \underset{\text{(II)}}{R_2C{:}CHX}$$

where X is an alkoxycarbonyl or cyano-group. There is considerable evidence [2] that bivalent sulphur stabilises an adjacent carbanion, suggesting that a thioalkyl or thioaryl group acts as an activating group X in the phosphonate olefin synthesis. Since vinyl thioethers (II; X = SR) which would be the product of such a reaction are hydrolysed

[1] Horner, Hoffmann, and Wippel, *Chem. Ber.*, 1958, **91**, 61; Horner, Hoffmann, Wippel, and Klahre, *ibid.*, 1959, **92**, 2499; Emmons and Wadsworth, *J. Amer. Chem. Soc.*, 1961. **83**, 1733.
[2] Cilento, *Chem. Rev.*, 1960, **60**, 149.

by aqueous acidic mercuric chloride to the corresponding carbonyl compound,[3] dialkyl alkyl- or aryl-thiomethylphosphonates (I; X = SR') might be useful reagents for effecting the transformation $>C{=}O \longrightarrow >CH{\cdot}CHO$, providing an alternative to the glycidic ester sequence [4] or the reaction of carbonyl compounds with methoxy- or methylthio-methyltriphenylphosphoranes.[5]

Dialkyl alkyl- and aryl-thiomethylphosphonates appear not to have been previously prepared. Phenylthiomethyl chloride, when heated with triethyl phosphite, gave one product which on the basis of the infrared spectrum, elemental analysis and molecular-weight measurements can be assigned the structure (I; X = SPh, R = Et); that the product was not *S*-benzyl diethyl phosphorothiolate was proved by comparison with an authentic sample. Methylthiomethyl chloride in benzene as solvent underwent a complex reaction with triethyl phosphite; distillation of the reaction mixture gave two main fractions. The lower-boiling was shown to be a 1 : 1 mixture of triethyl phosphorothionate and triethyl phosphate by gas chromatography and comparison of the infrared spectra with authentic samples. There was no evidence for the formation of diethyl ethylphosphonate. The infrared spectrum, elemental analysis, and molecular weight of the higher-boiling fraction, which was shown to be homogeneous by gas chromatography, agreed with structure (I; R = Et, X = SMe). When the reaction was run in the absence of a solvent, the yield of the required product (I) was almost doubled, with a corresponding decrease in the abnormal products triethyl phosphate and triethyl phosphorothioate. In view of the complexity of this reaction further evidence for the structure of the high-boiling product was sought. The proton magnetic resonance spectrum supported the structural assignment.

Diethyl phenyl- and methyl-thiomethylphosphonate both failed visibly to react with a suspension of sodium hydride in ethylene glycol dimethyl ether. However, simultaneous addition of the phosphorus compound and a carbonyl compound resulted in reaction, as shown by gas evolution, dissolution of the sodium hydride, and formation of the vinyl sulphide.

The rate of reaction was observed to be dependent on the structure of the carbonyl compound. The results obtained are summarised in the Table.

The dependence of the reaction of an ester (I) with sodium hydride on the presence of a carbonyl compound, and the dependence of its rate on the structure of the carbonyl compound, limit the value of this reaction as a synthetic method.

To confirm that the sulphur atom in compounds of the type (I) activates the α-hydrogen atom, the corresponding oxygen compound, *i.e.*, diethyl methoxymethylphosphonate, was prepared by reaction of chloromethyl methyl ether with triethyl phosphite and was recovered unchanged after being refluxed with sodium hydride in the presence of benzaldehyde.

| Carbonyl compound | Rate of reaction | Yield (%) of vinyl sulphide |
|---|---|---|
| Pinacolone | No reaction | — |
| Benzaldehyde | Very rapid | 65 |
| α-Naphthaldehyde | Rapid | 60 |
| Acetophenone | Slow | 43 |
| Benzophenone | Very slow | 35 |

In contrast with the reported [6] lability of the methylthiomethyl group in the reaction of methylthiomethyltriphenylphosphonium chloride with alkali, gas chromatography demonstrated the absence of triethyl phosphate after diethyl methylthiomethylphosphonate had been refluxed with 0·5M-sodium ethoxide in ethanol for 24 hours. Attempts

[3] Arens and Weiland, *Rec. Trav. chim.*, 1960, **79**, 1293.
[4] Houben-Weil, "Methoden der Organischen Chemie," Vol. VII, Part I, Georg Thieme Verlag, Stuttgart, 1954, p. 326.
[5] Levine, *J. Amer. Chem. Soc.*, 1958, **80**, 6150; Wittig and Schlosser, *Chem. Ber.*, 1961, **94**, 1373.
[6] Schlosser, *Angew. Chem.*, 1962, **74**, 291.

to obtain sulphonium salts from diethyl methylthiomethylphosphonate were unsuccessful. Ethyl bromide failed to react at 160° in a sealed tube; ethyl iodide reacted slowly under these conditions to yield diethylmethylsulphonium iodide.

*Experimental.*—Molecular weights were determined in benzene.

*Diethyl phenylthiomethylphosphonate.* Phenylthiomethyl chloride (39·8 g.) was added dropwise with stirring to triethyl phosphite (41·5 g.). No reaction occurred. The mixture was heated at 110° for 24 hr. Distillation gave *diethyl phenylthiomethylphosphonate* (75%), b. p. 126—128°/0·4 mm., $n_D^{20}$ 1·5350 (Found: C, 50·3; H, 6·7; S, 12·7; P, 11·9%; *M*, 256. $C_{11}H_{17}O_3PS$ requires C, 50·7; H, 6·6; S, 12·3; P, 11·9%; *M*, 260), $\nu_{max.}$ 8·05 (P=O), 8·65 and 9·8 μ (P·OEt).

*Diethyl methylthiomethylphosphonate.* Methylthiomethyl chloride (48·3 g.) was added dropwise with stirring to triethyl phosphite (83·0 g.). Heat was evolved. The mixture was heated at 110° for 6 hr. Distillation gave a first fraction (20 g.) b. p. 90—91°/14 mm., identified as a 1 : 1 mixture of triethyl phosphate and triethyl phosphorothionate by gas chromatography (Perkin-Elmer silicone column type " O "). The second fraction, *diethyl methylthiomethylphosphonate* (45 g.), had b. p. 70—72°/0·2 mm., $n_D^{20}$ 1·4635 (Found: C, 36·6; H, 7·7; S, 15·8; P, 15·4%; *M*, 200. $C_6H_{15}O_3PS$ requires C, 36·4; H, 7·6; S, 16·2; P, 15·6%; *M*, 198), $\nu_{max.}$ 8·05 (P=O), 8·65, 9·8 μ (P·OEt). The proton magnetic resonance spectrum measured at 60 Mc./sec. in carbon tetrachloride solutions with tetramethylsilane as internal reference showed peaks centred at 8·65 (triplet, 6 protons) ($CH_3$·$CH_2$·O), 7·72 (singlet, 3 protons) ($CH_3$·S), 7·42 (doublet, 2 protons) (P·$CH_2$), and 5·83 τ (quintet, 4 protons) ($CH_3$·$CH_2$·O).

*Diethyl methoxymethylphosphonate.* A mixture of chloromethyl methyl ether (16·1 g.) and triethyl phosphite (32·2 g.) was heated at 110° for 24 hr. Distillation gave *diethyl methoxymethylphosphonate* (85%), b. p. 65—67°/0·1 mm., $n_D^{20}$ 1·4210 (Found: C, 39·9; H, 8·4; P, 16·6%; *M*, 187. $C_6H_{15}O_4P$ requires C, 39·6; H, 8·3; P, 17·0%; *M*, 182), $\nu_{max.}$ 8·0 (P=O), 8·6 and 9·8 μ (P·OEt).

*2,2-Diphenylvinyl methyl sulphide.* Diethyl methylthiomethylphosphonate (19·8 g.) and benzophenone (18·2 g.) in ethylene glycol dimethyl ether (100 ml.) were added to a suspension of sodium hydride (50% in oil) (4·8 g.). No reaction occurred. The mixture was heated at 50—60° for 15 min.; the sodium hydride dissolved with gas evolution. The solvent was removed under reduced pressure, and the residue dissolved in ethyl acetate (100 ml.), washed with water (3 × 50 ml.), and dried ($MgSO_4$). Distillation of the residue after removal of solvent gave 2,2-diphenylvinyl methyl sulphide (35%), b. p. 115—120°/0·1 mm., m. p. 73° (from ethanol) (lit.,[5] 74°) (Found: C, 79·5; H, 5·6; S, 13·9%; *M*, 220. Calc. for $C_{15}H_{14}S$: C, 79·6; H, 6·2; S, 14·2%; *M*, 226).

The following reactions were carried out on a 0·1 molar scale essentially as described above. Benzaldehyde and diethyl methylthiomethylphosphonate with sodium hydride gave immediately methyl 2-phenylvinyl sulphide (65%), b. p. 66—67°/0·05 mm. (lit.,[5] b. p. 126—127°/12 mm.), $n_D^{20}$ 1·6325 (Found: C, 71·9; H, 6·7; S, 20·9%; *M*, 142. Calc. for $C_9H_{10}S$: C, 72·0; H, 6·7; S, 21·3%; *M*, 150). α-Naphthaldehyde at room temperature in 2 hr. gave *methyl 1-1′-naphthylvinyl sulphide* (60%), b. p. 120—122°/0·1 mm., $n_D^{20}$ 1·6610 (Found: C, 77·9; H, 6·4; S, 15·5%; *M*, 191. $C_{13}H_{12}S$ requires C, 78·0; H, 6·0; S, 16·0%; *M*, 200). Acetophenone at room temperature in 5 hr. gave *methyl 2-phenylpropenyl sulphide* (43%), b. p. 70—72°/0·1 mm., $n_D^{20}$ 1·6040 (Found: C, 73·0; H, 7·4; S, 19·3%; *M*, 173. $C_{10}H_{12}S$ requires C, 73·1; H, 7·4; S, 19·5%; *M*, 164).

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CYANAMID EUROPEAN RESEARCH INSTITUTE, 91 ROUTE DE LA CAPITE,
COLOGNY-GENEVA, SWITZERLAND.

[Present address: DEPARTMENT OF CHEMISTRY,
THE MANCHESTER COLLEGE OF SCIENCE AND TECHNOLOGY. [*Received, August 24th*, 1962.]

## 251. *The Infrared Spectroscopic Identification of the* P-*Methyl Group in Tertiary Phosphines.*

By K. B. Mallion, F. G. Mann, B. P. Tong, and V. P. Wystrach.

In the record of an extensive infrared spectroscopic study of " Sulphur-containing Organic Derivatives of Phosphorus Pyroacids," McIvor, Grant, and Hubley [1] briefly note that various phosphoric compounds containing the PMe or PEt group show bands in the region of 910—665 cm.$^{-1}$ which are " fairly constant and may be useful for verifying the presence of such a group." Inspection of their results shows that compounds of the " phosphoric " type having specifically the PMe group show a band in the 920—893 cm.$^{-1}$ region (Table 1; all bands in Tables are quoted in cm.$^{-1}$).

Table 1.

| | | | | | |
|---|---|---|---|---|---|
| Me·POCl$_2$ | 893 | Me·PO(OEt)$_2$ | 901 * | Me·POCl·O·C$_6$H$_{11}$ | 893 |
| Me·PSCl$_2$ | 909 | Me·PO(OPr$^i$)$_2$ | 901 * | MePr$^i$PSCl | 896 |
| Me·PO(OMe)$_2$ | 911 * | Me·PO(OBu$^n$)$_2$ | 921 | Me·PS(OPr$^i$)$_2$ | 909 |

* Meyrick and Thompson, *J.*, 1950, 225.

In the course of another investigation,[2] we have found that tertiary phosphines containing the PMe group show a sharp band of medium-strong intensity in the 880—875 cm.$^{-1}$ region (Table 2), which has a far more constant value than those of the above " phosphoric " compounds.

Table 2.

| | | | | | |
|---|---|---|---|---|---|
| Ph(CH$_2$·CH$_2$·CN)PMe | 880 | (*p*-Me·C$_6$H$_4$)$_2$PMe | 875 | (*m*-MeO·C$_6$H$_4$)PhPMe | 877 |
| Ph$_2$PMe | 877 | (*o*-MeO·C$_6$H$_4$)$_2$PMe | 879 | (*p*-MeO·C$_6$H$_4$)PhPMe | 880 |
| (*o*-Me·C$_6$H$_4$)$_2$PMe | 878 | (*o*-MeO·C$_6$H$_4$)PhPMe | 876 | | |

This rocking frequency band is not shown by tertiary phosphines having the PEt group: for example, Ph$_2$PEt shows no band in this region. It is not shown decisively by tertiary phosphines having the PMe$_2$ group: thus PhPMe$_2$ shows triple bands at 938m, 893m, and 863w cm.$^{-1}$.

Compounds containing an NMe or NMe$_2$ group show a characteristic band in the region 2820—2760 cm.$^{-1}$ region, but the band disappears when the nitrogen group undergoes oxidation, salt formation, co-ordination to metals, or even amide formation with charge separation.[3]

The effect on the 875—880 cm.$^{-1}$ P-methyl rocking frequency of similar changes in the above tertiary phosphines has therefore been briefly investigated. In Table 3, the bands over the wider range 916—860 cm.$^{-1}$ are recorded.

Table 3.

| | | | |
|---|---|---|---|
| (*o*-MeO·C$_6$H$_4$)PhMePO | 878s, 863w | [Ph$_3$MeP]I | 916s, 907s |
| (*m*-MeO·C$_6$H$_4$)PhMePO | 902sh, 889m * | [(*o*-Me·C$_6$H$_4$)$_3$MeP]I | 902sh, 890m |
| (*p*-MeO·C$_6$H$_4$)PhMePO | 885m * | [(*m*-Me·C$_6$H$_4$)$_3$MeP]I | 890vw, 865vw,br |
| (*o*-MeO·C$_6$H$_4$)PhMeP→AuBr | 889s, 899w | [(*p*-Me·C$_6$H$_4$)$_3$MeP]I | 905s |
| (*o*-MeO·C$_6$H$_4$)PhMeP→AuBr$_3$ | 893s, 903m | | |
| (*m*-MeO·C$_6$H$_4$)PhMeP→AuBr$_3$ | 894m, 904m | | |

* Material not crystalline.

There is a general shift to higher wave numbers in this series (as in Table 1), with the striking exception of the oxide of *o*-methoxyphenylmethylphenylphosphine, in which the oxide and the parent phosphine have similar bands at 878 and 876 cm.$^{-1}$, respectively.

The presence of a band in the 880—875 cm.$^{-1}$ region must, however, be interpreted

[1] McIvor, Grant, and Hubley, *Canad. J. Chem.*, 1956, **34**, 1611.
[2] Mann, Tong, and Wystrach, *J.*, 1963, 1155.
[3] Braunholtz, Ebsworth, Mann, and Sheppard, *J.*, 1958, 2780.

with care. Secondary phosphines often have, in addition to the " normal " band in the 2290—2280 cm.$^{-1}$ region, a band in the 900—880 cm.$^{-1}$ region. A few examples are recorded in Table 4.

TABLE 4.

| | | | |
|---|---|---|---|
| $Ph_2PH$ | 2280s, 998m | (*m*-EtO·$C_6H_4$)PhPH | 2280m, 886vw |
| (*o*-Cl·$C_6H_4$)PhPH | 2280m, 897m | (*p*-EtO·$C_6H_4$)PhPH | 2290m, 890m |
| (*o*-Br$C_6H_4$)PhPH | 2290m, 893s | (*m*-Me·$C_6H_4$)PhPH | 2290m, 888m |
| (*m*-MeO·$C_6H_4$)PhPH | 2280m, 895m | (3,5-$Me_2C_6H_3$)PhPH | 2280m, 887m |

The values of the P–H angle deformation frequencies here are all above 880 cm.$^{-1}$; further, the chemical properties of secondary phosphines and the tertiary arylmethylphosphines are so obviously distinct that no confusion can readily arise.

The only tertiary alkyldiarylphosphine encountered which has no PMe group but has a band in the 880—875 cm.$^{-1}$ range is methyl (*m*-methoxyphenylphenylphosphino)acetate, (*m*-MeO·$C_6H_4$)PhP·$CH_2$·$CO_2$Me, which has a band at 881 cm.$^{-1}$; the corresponding acid has a band at 896 cm.$^{-1}$.[2]

We would suggest, therefore, that a band in the 880—875 cm.$^{-1}$ region in the spectrum of a tertiary phosphine is a strong indication of the presence of a PMe group, and is of considerable diagnostic value when other groups in the molecule mask the " normal " band for the PMe group in the 1290—1280 cm.$^{-1}$ region:[4] the converse can be stated more strongly, namely that the absence of such a band in the spectrum of a tertiary phosphine shows the absence of this group.

*Experimental.*—The preparation of the methoxyphenylmethylphenylphosphines and their derivatives is described in ref. 2.

The following phosphines were prepared by the action of an excess of the appropriate arylmagnesium bromide on methylphosphonous dichloride. *Methyldi-o-tolylphosphine*, m. p. 54—54·5° (from ethanol) (Found: C, 79·3; H, 7·8. $C_{15}H_{17}P$ requires C, 78·9; H, 7·5%). Methyldi-*p*-tolylphosphine, b. p. 125—127°/0·45 mm. (lit.,[5] 345°). *Methyldi-o-methoxyphenylphosphine*, m. p. 121—123° (from ethanol) (Found: C, 68·9; H, 7·0. $C_{15}H_{17}O_2P$ requires C, 69·2; H, 6·6%).

Quaternary salts were prepared by the union of the tertiary phosphines and methyl iodide in hot toluene solution, from which the salts rapidly separated. *Methyltri-o-tolylphosphonium iodide*, recrystallised from water and dried at 90°/0·1 mm. for 3 hr., formed a *hemihydrate*, m. p. 233—234° (Found: C, 58·45; H, 5·4. $C_{22}H_{24}IP,\frac{1}{2}H_2O$ requires C, 58·2; H, 5·5%): further drying at 120°/0·1 mm. for 6 hr. gave the anhydrous salt, of unchanged m. p. (Found: C, 58·8; H, 5·2. $C_{22}H_{24}IP$ requires C, 59·2; H, 5·4%). Infrared spectra showed the presence of a hydroxyl group in the former and not in the latter. *Methyltri*-m-*tolylphosphonium iodide*, m. p. 162° after drying at 90°/0·1 mm., was recrystallised from water containing sufficient ethanol to prevent separation of the liquid salt (Found: C, 59·25; H, 5·5. $C_{22}H_{24}IP$ requires C, 59·2; H, 5·4%). *Methyltri*-p-*tolylphosphonium iodide* had m. p. 191—192° after crystallisation from water and drying at 100°/0·2 mm. (Found: C, 59·5; H, 5·7. $C_{22}H_{24}IP$ requires C, 59·2; H, 5·4%).

We are indebted to Mr. M. J. Gallagher and Dr. E. C. Kirby for the values of certain secondary phosphines (Table 4) which they had prepared. We gratefully acknowledge grants from the Department of Scientific and Industrial Research (to K. B. M. and B. P. T.), and a Senior Educational Award by the American Cyanamid Company (to V. P. W.).

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, August 27th*, 1962.]

[4] Thomas, *Chem. and Ind.*, 1957, 198.
[5] Michaelis, *Annalen*, 1901, **315**, 43.

## 252. *Some Derivatives of 4-Acetamidonaphthalene-1-sulphonyl Hydrazide.*

By R. J. W. Cremlyn.

The various derivatives of 4-acetamidonaphthalene-1-sulphonyl hydrazide listed in the annexed Tables have been prepared as potential bactericides. The methods used were standard and are indicated in the Experimental section. But all attempts to obtain the hydrazones of benzophenone, benzoin, and camphor proved unsuccessful. Many trichloromethylthio-derivatives are fungicidal,[1] and in particular good activity has been reported [2] for certain aryloxy-compounds of type $Ar{\cdot}O{\cdot}S{\cdot}CCl_3$. Accordingly, the hydroxysulphonylhydrazones were condensed with trichloromethanesulphenyl chloride, and the products tested for fungitoxicity. Efforts were made to discover an effective method of characterising the naphthalenesulphonyl hydrazide derivatives. Chromatography was of little value (cf. ref. 3). However, an absorption band at 300—302 mμ (ε 9000—11,000) characterises the aliphatic 4-acetamidonaphthalene-1-sulphonylhydrazones; with the aromatic analogues the band is at 305—310 mμ (ε 21,000—25,000); and for the 1-acylamidosulphonyl hydrazides is at 260—265 mμ (ε 7000—9000).

*Experimental.*—M. p.s were determined by using sealed tubes (to minimise decomposition).

4-Acetamidonaphthalene-1-sulphonyl chloride has been previously prepared: (*a*) by treating sodium *N*-acetylnaphthionate with phosphorus pentachloride [4] and (*b*) by the action of chlorosulphonic acid on α-acetamidonaphthalene.[5] In this work method (*b*) was used, but at 60—65° for 2 hr. which raised the yield to 45% (cf. Goldyrev and Postovskii [5]).

The sulphonyl chloride (15 g.) in ether (250 c.c.) was added to a stirred mixture of 98% hydrazine hydrate (12 g.) and sodium hydrogen carbonate (12 g.) in methanol (20 c.c.). The suspension was shaken for 1 hr., left overnight, and filtered. The solid was washed with water, ice-cold methanol, and ether, and dried at room temperature, yielding the pure hydrazide (10 g.), m. p. 161—162° (decomp.) (lit.,[5] m. p. 162°) (Found: C, 51·5; H, 4·6; S, 11·6. Calc. for $C_{12}H_{13}N_3O_3S$: C, 51·6; H, 4·7; S, 11·5%). This procedure gives a cleaner product than the original method.[6]

*4-Acetamidonaphthalene-1-sulphonylhydrazones* (Tables 1 and 2) were prepared by heating the hydrazide and aldehyde or ketone in ethanol. The products were purified by rapid recrystallisation from boiling ethanol. For the preparation of the derivative from glucose, acetonitrile had to be used as solvent (cf. ref. 7).

*4-Acylamidonaphthalene-1-sulphonyl hydrazides* (Table 4). The α-acylaminonaphthalenes were obtained from α-naphthylamine by treatment with the appropriate acyl chloride in ether, followed by the addition of aqueous sodium hydroxide.[8] The solid material was filtered off and recrystallised from methanol; it was then converted into the corresponding sulphonylhydrazide as previously described.

*N-Substituted 4-acetamidonaphthalene-1-sulphonyl hydrazides* (Table 3). 4-Acetamidonaphthalene-1-sulphonyl hydrazide was treated with the acyl or sulphonyl chloride (1·5 mol.) in cold pyridine; the solution was left overnight and then worked up in the usual manner.

*Condensation with trichloromethanesulphenyl chloride.* The hydroxy-sulphonylhydrazone was dissolved in 2N-sodium hydroxide, and an excess of the sulphenyl chloride was dropped into the stirred solution at 0°. After ½ hour's stirring, the solid product was filtered off and recrystallised from methanol. This reaction was performed with the sulphonylhydrazones

[1] Kittleson, *Science*, 1952, **115**, 84; Johnston, Rueggeberg, and Block, *J. Sci. Food Agric.*, 1957, **5**, 672; Pfleger, *Angew. Chem.*, 1953, **65**, 415.
[2] Fawcett, Spencer, and Wain, *Ann. Appl. Biol.*, 1958, **46**, 651.
[3] Cremlyn, *J.*, 1962, 2133.
[4] Knüsli, Thesis, E.T.H., Zürich, 1948, p. 81; Minoru Hiyama, *J. Pharm. Soc. Japan*, 1952, **72**, 1370; Schroeter, *Ber.*, 1906, **39**, 1564.
[5] Goldyrev and Postovskii, *J. Appl. Chem.* (*U.S.S.R*), 1938, **11**, 316.
[6] Takeo Ueda *et al.*, Jap P. 4228/1956.
[7] Westphal, Feier, Lüderitz, and Fromme, *Biochem. Z.*, 1954, **326**, 139.
[8] Toyozo Takada, Jap. P. 6879/1955.

TABLE 1.

Aldehyde 4-acetamidonaphthalene-1-sulphonylhydrazones, $Ac{\cdot}NH{\cdot}C_{10}H_6{\cdot}SO_2{\cdot}NH{\cdot}N{=}CHR$.

| R | M. p. | Formula | Found (%) C | H | N | S | Required (%) C | H | N | S |
|---|---|---|---|---|---|---|---|---|---|---|
| *(a) From aliphatic aldehydes.* | | | | | | | | | | |
| H * | 130—134° | $C_{13}H_{13}N_3O_3S$ | 53·4 | 4·6 | — | 10·7 | 53·6 | 4·5 | — | 11·0 |
| Me | 189—190 | $C_{14}H_{15}N_3O_3S$ | 54·8 | 5·0 | — | 10·35 | 55·1 | 4·9 | — | 10·5 |
| Et | 168—170 | $C_{15}H_{17}N_3O_3S$ | 55·8 | 5·2 | — | 9·5 | 56·4 | 5·3 | — | 10·0 |
| $Pr^n$ | 193—195 | $C_{16}H_{19}N_3O_3S$ | 57·3 | 5·2 | — | 10·0 | 57·7 | 5·7 | — | 9·6 |
| $Pr^i$ | 155—156 | $C_{16}H_{19}N_3O_3S$ | 57·8 | 5·8 | 12·1 | 8·7 | 57·7 | 5·7 | 12·6 | 9·6 |
| $Me{\cdot}CH{=}CH$ | 183—185 | $C_{16}H_{17}N_3O_3S$ | 57·6 | 5·7 | — | 9·1 | 58·0 | 5·1 | — | 9·7 |
| $n\text{-}C_6H_{13}$ | 146—147 | $C_{19}H_{25}N_3O_3S$ | 59·6 | 6·9 | — | 8·3 | 60·8 | 6·7 | — | 8·5 |
| $EtO_2C{\cdot}CH_2{\cdot}CH(CO_2Et)$ | 116—118 | $C_{19}H_{25}N_3O_7S$ | 51·2 | 5·5 | — | 7·0 | 51·9 | 5·6 | — | 7·3 |
| $HO{\cdot}CH_2{\cdot}[CH(OH)]_4$ | 142 | $C_{18}H_{23}N_3O_8S$ | 49·12 | 4·8 | — | 7·6 | 49·0 | 5·2 | — | 7·25 |
| *(b) From aromatic aldehydes.* | | | | | | | | | | |
| Ph | 219° | $C_{19}H_{17}N_3O_3S$ | 62·0 | 4·8 | — | 8·8 | 62·1 | 4·6 | — | 8·7 |
| $o\text{-}Cl{\cdot}C_6H_4$ | 226 | $C_{19}H_{16}ClN_3O_3S$ | 56·9 | 4·0 | — | 7·85 | 56·8 | 4·0 | — | 8·0 |
| $p\text{-}Cl{\cdot}C_6H_4$ | 216 | $C_{19}H_{16}ClN_3O_3S$ | 56·5 | 4·15 | — | 7·9 | 56·8 | 4·0 | — | 8·0 |
| $o\text{-}NO_2{\cdot}C_6H_4$ | 197 | $C_{19}H_{16}N_4O_5S$ | 55·6 | 3·8 | — | 7·6 | 55·3 | 3·9 | — | 7·8 |
| $p\text{-}NO_2{\cdot}C_6H_4$ | 230—231 | $C_{19}H_{16}N_4O_5S$ | 55·0 | 3·9 | — | 7·6 | 55·3 | 3·9 | — | 7·8 |
| $m\text{-}NO_2{\cdot}C_6H_4$ | 220 | $C_{19}H_{16}N_4O_5S$ | 55·25 | 4·0 | — | 7·4 | 55·3 | 3·9 | — | 7·8 |
| $2,4\text{-}(NO_2)_2C_6H_3$ | 110 | $C_{19}H_{15}N_5O_7S$ | 50·6 | 3·7 | — | 6·65 | 50·0 | 3·3 | — | 7·0 |
| $p\text{-}MeO{\cdot}C_6H_4$ | 208 | $C_{20}H_{19}N_3O_4S$ | 60·4 | 4·85 | — | 8·0 | 60·45 | 4·8 | — | 8·1 |
| 2-Furyl | 215 | $C_{17}H_{15}N_3O_4S$ | 56·9 | 4·35 | — | 8·65 | 57·1 | 4·2 | — | 9·0 |
| $p\text{-}Me_2N{\cdot}C_6H_4$ † | 218—220 | $C_{21}H_{22}N_4O_3S$ | 60·95 | 5·8 | — | 7·3 | 61·5 | 5·4 | — | 7·8 |
| $Ph{\cdot}CH{=}CH$ | 198—200 | $C_{21}H_{19}N_3O_3S$ | 64·6 | 5·0 | — | 7·6 | 64·1 | 4·8 | — | 8·1 |
| $p\text{-}NO_2{\cdot}C_6H_4CH{=}CH$ | 176—180 | $C_{21}H_{18}N_4O_5S$ | 56·8 | 4·2 | — | 6·9 | 57·4 | 4·1 | — | 7·3 |
| $Ph{\cdot}CH_2$ | 151—152 | $C_{20}H_{19}N_3O_3S$ | 62·7 | 5·15 | — | 8·4 | 63·0 | 5·0 | — | 8·4 |
| $o\text{-}HO{\cdot}C_6H_4$ | 134—135 | $C_{19}H_{17}N_3O_4S$ | 61·2 | 4·75 | — | 7·1 | 59·5 | 4·4 | — | 8·35 |
| $2\text{-}HO{\cdot}C_{10}H_6$ | 230 | $C_{23}H_{19}N_3O_4S$ | 63·4 | 4·2 | — | 7·8 | 63·7 | 4·4 | — | 7·4 |
| 3-MeO, 4-$HO,C_6H_3$ | 214—215 | $C_{20}H_{19}N_3O_5S$ | 58·25 | 4·8 | — | 7·6 | 58·1 | 4·6 | — | 7·75 |

† A canary-yellow solid.

TABLE 2.

Ketone 4-acetamidonaphthalene-1-sulphonylhydrazones, $Ac{\cdot}NH{\cdot}C_{10}H_6{\cdot}SO_2{\cdot}NH{\cdot}N{=}CRR'$.

| R | R′ | M. p. | Formula | Found (%) C | H | N | S | Required (%) C | H | N | S |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *(a) From aliphatic ketones.* | | | | | | | | | | | |
| Me | Me | 200—201° | $C_{15}H_{17}N_3O_3S$ | 56·2 | 5·7 | 13·2 | — | 56·4 | 5·3 | 13·2 | — |
| Me | Et | 202—203 | $C_{16}H_{19}N_3O_3S$ | 57·7 | 5·8 | 13·35 | — | 57·7 | 5·7 | 12·6 | — |
| Et | Et | 184—185 | $C_{17}H_{21}N_3O_3S$ | 57·9 | 6·2 | 12·2 | — | 58·8 | 6·05 | 12·1 | — |
| Me | $Pr^n$ | 186—188 | $C_{17}H_{21}N_3O_3S$ | 58·9 | 5·9 | 11·9 | — | 58·8 | 6·05 | 12·1 | — |
| Me | $Bu^i$ | 195 | $C_{18}H_{23}N_3O_3S$ | 59·4 | 6·2 | 11·3 | — | 59·8 | 6·4 | 11·6 | — |
| Me | $n\text{-}C_6H_{13}$ | 174—176 | $C_{20}H_{27}N_3O_3S$ | 61·7 | 6·6 | 10·75 | — | 61·7 | 6·9 | 10·8 | — |
| Me | $n\text{-}C_7H_{15}$ | 167·5 | $C_{21}H_{29}N_3O_3S$ | 62·1 | 7·2 | — | 8·0 | 62·5 | 7·2 | — | 7·9 |
| $-[CH_2]_4-$ | | 189—190 | $C_{17}H_{19}N_3O_3S$ | 59·6 | 5·8 | 12·4 | — | 59·1 | 5·5 | 12·2 | — |
| $-[CH_2]_5-$ | | 193 | $C_{18}H_{21}N_3O_3S$ | 59·9 | 5·55 | 11·95 | — | 60·2 | 5·85 | 11·7 | — |
| $-[CH_2]_6-$ | | 203—204 | $C_{19}H_{23}N_3O_3S$ | 60·2 | 5·9 | 10·4 | — | 61·4 | 6·2 | 11·25 | — |
| Me | $EtO_2C{\cdot}CH_2$ | 173—175 | $C_{18}H_{21}N_3O_5S$ | 55·0 | 5·5 | — | 8·3 | 55·2 | 5·4 | — | 8·2 |
| Me | $HO_2C$ | 217 | $C_{15}H_{15}N_3O_5S$ | 51·8 | 4·4 | — | 8·9 | 51·6 | 4·3 | — | 9·2 |
| *(b) From aromatic ketones.* | | | | | | | | | | | |
| Me | Ph | 227° | $C_{20}H_{19}N_3O_3S$ | 62·9 | 4·7 | 10·5 | — | 63·0 | 5·0 | 11·1 | — |
| Et | Ph | 212 | $C_{21}H_{21}N_3O_3S$ | 63·6 | 5·5 | — | 8·2 | 63·8 | 5·3 | — | 8·1 |
| Me | $p\text{-}Me{\cdot}C_6H_4$ | 218 | $C_{21}H_{21}N_3O_3S$ | 63·7 | 5·4 | — | 8·4 | 63·8 | 5·3 | — | 8·1 |
| Me | $p\text{-}HO{\cdot}C_6H_4$ | 242—243 | $C_{20}H_{19}N_3O_4S$ | 60·2 | 4·9 | — | 8·1 | 60·45 | 4·8 | — | 8·1 |
| Me | $p\text{-}Ph{\cdot}CO{\cdot}O{\cdot}C_6H_4$ | 212 | $C_{27}H_{23}N_3O_5S$ | 65·2 | 4·5 | — | 5·8 | 64·8 | 4·6 | — | 6·4 |
| Me | $p\text{-}Cl{\cdot}C_6H_4$ | 238 | $C_{20}H_{15}ClN_3O_3S$ | 58·4 | 3·3 | — | 7·35 | 58·2 | 3·6 | — | 7·75 |
| ‡ $-C_6H_4-NH{\cdot}CO-$ | | 219—220 | $C_{20}H_{16}N_4O_4S$ | 58·7 | 4·2 | — | 7·6 | 58·8 | 3·9 | — | 7·8 |
| $-C_6H_4{\cdot}C_6H_4-$ | | 239—240 | $C_{25}H_{18}N_3O_3S$ | 67·9 | 4·3 | — | 7·1 | 68·0 | 4·3 | — | 7·25 |

‡ Yellow plates (from EtOH).

TABLE 3.

Derivatives, $Ac{\cdot}NH{\cdot}C_{10}H_6{\cdot}SO_2{\cdot}NH{\cdot}NHX$.

| X | M. p. | Formula | Found (%) C | H | S | Required (%) C | H | S |
|---|---|---|---|---|---|---|---|---|
| Ph | 110—121° | $C_{18}H_{17}N_3O_3S$ | 60·2 | 4·9 | 8·5 | 60·85 | 4·8 | 9·0 |
| $NH_2{\cdot}CO$ | 214 | $C_{13}H_{14}N_4O_4S$ | 48·4 | 4·4 | 9·8 | 48·4 | 4·3 | 9·9 |
| Me·CO | 212—214 | $C_{14}H_{15}N_3O_4S$ | 52·1 | 4·7 | 9·9 | 52·3 | 4·7 | 10·0 |
| Ph·CO | 171—172 | $C_{19}H_{17}N_3O_4S$ | 59·0 | 5·35 | 7·9 | 59·5 | 4·4 | 8·35 |
| $Ph{\cdot}SO_2$ | 221 | $C_{18}H_{17}N_3O_5S_2$ | 51·2 | 4·3 | 15·8 | 51·55 | 4·05 | 15·3 |
| $p$-$Me{\cdot}C_6H_4{\cdot}SO_2$ | 116—117 | $C_{19}H_{19}N_3O_5S_2$ | 52·5 | 4·7 | 14·3 | 52·65 | 4·4 | 14·8 |
| Ph·NHCO | 218—220 | $C_{19}H_{18}N_4O_4S$ | 56·9 | 4·8 | 7·55 | 57·3 | 4·5 | 8·0 |

TABLE 4.

4-Acylamidonaphthalene-1-sulphonyl hydrazides and derivatives,

$R{\cdot}CO{\cdot}NH{\cdot}C_{10}H_6{\cdot}SO_2{\cdot}NH{\cdot}NH_2$.

| R | M. p. | Formula | Found (%) C | H | S | Required (%) C | H | S |
|---|---|---|---|---|---|---|---|---|
| $Bu^n$ | 157—158° | $C_{14}H_{17}N_3O_3S$ | 54·45 | 5·55 | 10·5 | 54·7 | 5·5 | 10·4 |
| Acetone hydrazone | 194—196 | $C_{17}H_{21}N_3O_3S$ | 59·1 | 6·15 | 9·3 | 58·8 | 6·05 | 9·2 |
| Benzaldehyde hydrazone | 212—214 | $C_{21}H_{21}N_3O_3S$ | 64·0 | 5·3 | 7·6 | 63·8 | 5·3 | 8·1 |
| Benzenesulphonyl deriv. | 210—211 | $C_{20}H_{21}N_3O_5S_2$ | 54·0 | 4·8 | 13·8 | 53·7 | 4·7 | 14·3 |
| $n$-$C_5H_{11}CO$ | 159—160 | $C_{16}H_{21}N_3O_3S$ | 57·0 | 6·3 | 9·55 | 57·3 | 6·3 | 9·55 |
| Acetone hydrazone | 200—201 | $C_{19}H_{25}N_3O_3S$ | 60·6 | 6·7 | 8·4 | 60·8 | 6·7 | 8·5 |
| Benzaldehyde hydrazone | 210 | $C_{23}H_{25}N_3O_3S$ | 64·5 | 6·1 | 7·4 | 65·25 | 5·9 | 7·55 |
| Glucose hydrazone | 150—152 | $C_{22}H_{31}N_3O_8S$ | 52·8 | 6·0 | 6·1 | 53·1 | 6·2 | 6·4 |
| Ph·CO | 176—178 | $C_{17}H_{15}N_3O_3S$ | 59·4 | 4·55 | 9·3 | 59·8 | 4·4 | 9·4 |
| Acetone hydrazone | 218—220 | $C_{20}H_{19}N_3O_3S$ | 62·75 | 5·1 | 8·4 | 63·0 | 5·0 | 8·4 |
| Benzaldehyde hydrazone | 222—224 | $C_{24}H_{19}N_3O_3S$ | 67·5 | 4·6 | 7·5 | 67·1 | 4·4 | 7·45 |
| Glucose hydrazone | 133—134 | $C_{23}H_{25}N_3O_8S$ | 54·8 | 5·0 | 5·95 | 54·9 | 4·7 | 6·4 |
| Benzenesulphonyl deriv. | 196—198 | $C_{23}H_{19}N_3O_5S_2$ | 57·0 | 3·8 | 12·8 | 57·4 | 3·95 | 13·3 |
| $p$-$Me{\cdot}C_6H_4{\cdot}SO_2$ | 109—110 | $C_{17}H_{17}N_3O_4S_2$ | 51·3 | 4·8 | 17·0 | 52·2 | 4·35 | 16·4 |
| Acetone hydrazone | 158—159 | $C_{20}H_{21}N_3O_4S_2$ | 54·9 | 5·4 | 14·2 | 55·6 | 4·9 | 14·85 |
| Benzaldehyde hydrazone | 130—133 | $C_{24}H_{21}N_3O_4S_2$ | 60·5 | 5·0 | 12·8 | 60·1 | 4·4 | 13·4 |

from the following carbonyl compounds giving products with the cited m. p.s and analytical data: 2-hydroxynaphthaldehyde, 158—160° (Found: C, 46·7; H, 3·3; S, 13·0%); 4-hydroxy-3-methoxybenzaldehyde, 135—140° (Found: C, 38·2; H, 3·0; S, 14·4%); 4-hydroxyacetophenone, 142—143° (Found: C, 43·2; H, 3·3; S, 13·6%); *o*-hydroxybenzaldehyde, 130—132° (Found: C, 40·9; H, 2·8; S, 13·7%). The results appear to indicate that the products are mixtures of the mono- and bis-trichloro-methylthio-derivatives.

*Chromatography.* On paper chromatography with Whatman No. 1 paper and in the following solvent systems: (i) butan-1-ol, (ii) butan-1-ol–water (86 : 14); (iii) butan-1-ol–acetic acid–water (4 : 1 : 5); and (iv) butan-1-ol–aqueous ammonia (*d* 0·88)–water (4 : 1 : 5), the hydrazine derivatives after spraying with *p*-dimethylaminobenzaldehyde gave orange ultraviolet-fluorescent spots, mainly close to the solvent front, of $R_F$ values (i) 0·90—0·93, (ii) 0·89–0·93, (iii) 0·80—0·86 and 0·35—0·42, (iv) 0·81—0·83. In system (iii) the double spots are probably due to ionisation of the bases since they are not observed with the hydrazones. The latter were located directly by their ultraviolet fluorescence.

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HATFIELD COLLEGE OF TECHNOLOGY, ROE GREEN,
HATFIELD, HERTS.

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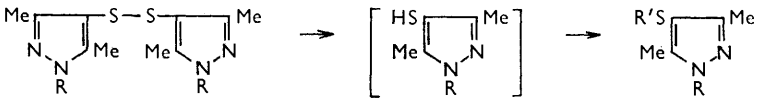
## 253. 4-*Mercaptopyrazoles.*

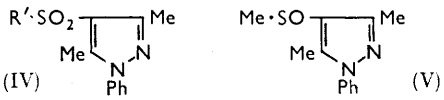
By D. L. Pain.

Substituted 4-mercaptopyrazoles (III) were prepared (for tests against *Mycobacterium tuberculosis*) by reductive fission of the disulphides (I), followed by alkylation (cf. Barry, Finar, and Simmonds,[1] who prepared 4-benzylthio-3-methyl-1,5-diphenylpyrazole and the corresponding sulphone by this method). The thiol (II; R = Ph) was too unstable to be



(I) (II) (III)

isolated, and alkylation was carried out *in situ*. The disulphides (I) were prepared [1] by the action of substituted hydrazines on bis-1-acetylacetonyl disulphide.[2] Isopropyl- and cyclohexyl-hydrazine were made [3] from the corresponding ketones.



(IV) (V)

The sulphones (IV; R′ = Me and Bu$^n$) were prepared by oxidation of the sulphides (III; R = Ph, R′ = Me and Bu$^n$) with hydrogen peroxide and acetic acid at 100° and chromium trioxide and acetic acid [4] at 50—55°, respectively, but the sulphoxide (V) could not be made by mild peroxide oxidation.

*Experimental.*—1-*Substituted* 4-*alkylthio*-3,5-*dimethylpyrazoles* (see Table). The disulphide (0·1 mole) in ethanol (650 ml.) and water (1300 ml.) containing sodium hydroxide (10 g.) and sodium dithionite (32 g.) was boiled under reflux with stirring for 1·5 hr. The alkylating agent (0·22 mole) was added and stirring and refluxing were continued for a further 0·5—17 hr. The ethanol was evaporated *in vacuo* and the *product* which separated from the aqueous residue was filtered off or extracted with ether or light petroleum (b. p. 40—60°). It was purified by distillation or by recrystallisation.

*Bis*-1-*isopropyl*-3,5-*dimethylpyrazol*-4-*yl disulphide*. Bis-1-acetylacetonyl disulphide (2·62 g.) was heated for 1 hr. at 100° with isopropylhydrazine (1·63 g.) in glacial acetic acid (10 ml.). Water was added to the cooled mixture, and the precipitated gum was separated by decantation. It was extracted with ether, and the extract was washed with aqueous sodium hydrogen carbonate, then with water and dried ($Na_2SO_4$) and the solvent was evaporated. The residual gum crystallised on trituration and recrystallised from a small volume of light petroleum (b. p. 60—80°) to give the *disulphide* (2·4 g., 71%), as pale yellow plates, m. p. 73—75° (Found: C, 56·9; H, 8·2; N, 16·7; S, 18·85. $C_{16}H_{26}N_4S_2$ requires C, 56·75; H, 7·75; N, 16·55; S, 18·95%).

*Bis*-1-*cyclohexyl*-3,5-*dimethylpyrazol*-4-*yl disulphide* was prepared similarly and crystallised from light petroleum (b. p. 60—80°) as yellow rhombs (61%), m. p. 109—109·5° (Found: C, 63·5; H, 8·2; N, 13·1; S, 15·3. $C_{22}H_{34}N_4S_2$ requires C, 63·15; H, 8·2; N, 13·4; S, 15·35%).

*Sodium* 3,5-*dimethyl*-1-*phenylpyrazol*-4-*ylthioacetate*. Treatment of 4-carboxymethylthio-3,5-dimethyl-1-phenylpyrazole (19·4 g., see Table) with N-sodium hydroxide (73·65 ml.) gave the *salt* (21·0 g., 100%), m. p. 256—257° (Found: N, 9·5; Na, 7·85; S, 11·0. $C_{13}H_{13}N_2NaO_2S$ requires N, 9·85; Na, 8·1; S, 11·3%).

3,5-*Dimethyl*-4-*methylsulphonyl*-1-*phenylpyrazole*. 3,5-Dimethyl-4-methylthio-1-phenylpyrazole (24 g.) in glacial acetic acid (240 ml.) was treated with hydrogen peroxide (100-vol.;

[1] Barry, Finar, and Simmonds, *J.*, 1956, 4974.
[2] Vaillant, *Compt. rend.*, 1894, **119**, 647.
[3] Lochte, Noyes, and Bailey, *J. Amer. Chem. Soc.*, 1922, **44**, 2556.
[4] Caldwell and Sayin, *J. Amer. Chem. Soc.*, 1952, **74**, 4314.

120 ml.) and heated on the steam-bath for 1 hr. The *sulphone* was precipitated from the cooled solution by dilution with water, collected, and crystallised from carbon tetrachloride, to give colourless needles (17 g., 62%), m. p. 122—123° (Found: N, 10·9; S, 12·75. $C_{12}H_{14}N_2O_2S$ requires N, 11·2; S, 12·8%).

*4-Butylsulphonyl-3,5-dimethyl-1-phenylpyrazole.* 4-Butylthio-3,5-dimethyl-1-phenylpyrazole (35·5 g.) in glacial acetic acid (410 ml.) was heated to 50°. Chromium trioxide (43·7 g.) in water (85 ml.) was added during 0·5 hr. with stirring. Stirring at 50—55° was continued for a further 0·5 hr. The mixture was cooled in ice, and the excess of oxidising agent was decomposed by sulphur dioxide. Dilution of the mixture with water gave an oil which was extracted with benzene. The extract was washed with aqueous sodium hydrogen carbonate and then with water, dried ($Na_2SO_4$), and evaporated. A solution of the residual gum in ether was heated with charcoal, filtered, and concentrated, and light petroleum (b. p. 40—60°) added to give the *sulphone* (19 g., 48%), m. p. 38—40°. Distillation at 185—190°/0·07 mm. caused considerable decomposition (Found: C, 62·3; H, 6·9; N, 9·2; S, 10·45. $C_{15}H_{20}N_2O_2S$ requires C, 61·6; H, 6·9; N, 9·6; S, 10·95%).

*Copper salt of bis-1-acetylacetonyl disulphide.* Bis-1-acetylacetonyl disulphide (26·2 g.) in ethanol (250 ml.) was mixed, with stirring, with ethanolic cupric acetate (39·9 g. of monohydrate in 1250 ml. of boiling ethanol, cooled, and filtered). Stirring was continued for a further 1 hr. and the mixture was left overnight. The pale green *salt* was collected, thoroughly washed with water, with ethanol and, finally with ether, and dried at 30—35° (yield, 30 g., 93%). It had m. p. 157° (decomp.; rapid heating) (Found: C, 36·75; H, 4·1; Cu, 19·5; S, 19·8. $C_{10}H_{12}CuO_4S_2$ requires C, 37·1; H, 3·75; Cu, 19·6; S, 19·8%).

1-Substituted 4-alkylthio-3,5-dimethylpyrazoles (III).

| No. | R | R′ | M. p. | B. p./mm. | Alkylating agent | Yield (%) | Crystallizing solvent | Appearance |
|---|---|---|---|---|---|---|---|---|
| 1 | Ph | Me | 95—96° | — | $Me_2SO_4$ | 97 | Light petroleum (b. p. 60—80°) | Blades |
| 2 | Ph | Et | — | 112°/0·04 | $Et_2SO_4$ | 56 | — | Oil |
| 3 | Ph | $Pr^i$ | — | 118—120°/0·02 | $Pr^iBr$ | 39 | — | Oil |
| 4 | Ph | $Bu^n$ | — | 140°/0·1 | $Bu^nBr$ | 86 | — | Oil |
| 5 | Ph | n-$C_{12}H_{25}$ | *ca.* 15 | 210—220°/0·02 | n-$C_{12}H_{25}Br$ | 74 | — | Plates |
| 6 | Ph | Ph·$CH_2$ | 27—28 | 165—170°/0·01 | Ph·$CH_2Cl$ | 45 | — | Yellow plates |
| 7 | Ph | $CH_2$·$CO_2H$ | 148—149 | — | Cl·$CH_2$·$CO_2H$ | 78 | $NH_4$·OH–HCl pptn. | Crystals |
| 8 | $Pr^i$ | Me | 35—37 | — | $Me_2SO_4$ | 62 | Light petroleum (b. p. 40—60°) | Needles |
| 9 | Cyclohexyl | Me | 60—61 | — | ,, | 87 | ,, | ,, |

| | Found (%) | | | | | Required (%) | | | |
|---|---|---|---|---|---|---|---|---|---|
| No. | C | H | N | S | Formula | C | H | N | S |
| 1 | — | — | 12·7 | 14·55 | $C_{12}H_{14}N_2S$ | — | — | 12·85 | 14·7 |
| 2 | 67·7 | 7·2 | 12·05 | 14·05 | $C_{13}H_{16}N_2S$ | 67·2 | 6·95 | 12·05 | 13·8 |
| 3 | 68·4 | 7·5 | 11·2 | 13·0 | $C_{14}H_{18}N_2S$ | 68·25 | 7·35 | 11·4 | 13·0 |
| 4 | 69·55 | 7·8 | 10·65 | 12·15 | $C_{15}H_{20}N_2S$ | 69·2 | 7·75 | 10·75 | 12·3 |
| 5 | 74·15 | 9·85 | 7·25 | 8·65 | $C_{23}H_{36}N_2S$ | 74·15 | 9·75 | 7·5 | 8·6 |
| 6 | 73·4 | 6·3 | 9·5 | 10·95 | $C_{18}H_{18}N_2S$ | 73·45 | 6·15 | 9·5 | 10·9 |
| 7 | 59·1 | 5·45 | 10·4 | 12·0 | $C_{13}H_{14}N_2O_2S$ | 59·5 | 5·4 | 10·7 | 12·25 |
| 8 | 58·7 | 8·85 | 15·2 | 17·5 | $C_9H_{16}N_2S$ | 58·65 | 8·75 | 15·2 | 17·4 |
| 9 | 64·5 | 9·1 | 12·55 | 14·25 | $C_{12}H_{20}N_2S$ | 64·25 | 9·0 | 12·5 | 14·3 |

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RESEARCH LABORATORIES, MAY & BAKER LTD.,
DAGENHAM, ESSEX.

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## 254. *Ester Exchange in the Hydrolysis of Diphenyl Terephthalate.*

By B. H. Chase.

Phenyl hydrogen terephthalate has not previously been described. The most promising route to it appeared to be by partial hydrolysis of the diphenyl ester, but treatment with slightly less than one equivalent of ethanolic potassium hydroxide gave ethyl hydrogen terephthalate. The low solubility of the diphenyl ester precluded the use of aqueous ethanol but hydrolysis in 90% 2-ethoxyethanol gave only the mono- and the bis-ethoxyethyl esters. The required ester was prepared by hydrolysis in 97% t-butyl alcohol or in phenol. It could be obtained more conveniently, together with the diphenyl ester, from technical terephthaloyl chloride and phenol.

The ester exchange presumably involves nucleophilic attack on the ester-carbonyl group by alkoxide ion, and the likelihood of such exchange accompanying hydrolysis therefore depends in part on the molar ratio of water present and on the acidity of the alcohol employed. Hine and Hine [1] studied the relative acidity of water and a range of alcohols in isopropanolic solution and record the following values for $K_e$ (= $[A^-]/[HA][Pr^iO^-]$): $H_2O$ 1·2, EtOH 0·95, $EtO{\cdot}CH_2{\cdot}CH_2{\cdot}OH$ 12, relative to $Pr^iOH$ 0·076.

Dissociation constants are likely to remain in the same sequence in other alcohols so that it is not surprising that in ethanol and in 90% 2-ethoxyethanol (*i.e.*, a molar ratio alcohol : water of 2 : 1) ester exchange is at least comparable in rate with hydrolysis. The use of propan-2-ol, a considerably weaker acid than water, might be expected to lead to much less ester exchange, but in fact hydrolysis gave only a mixture of mono- and di-isopropyl esters. The absence of exchange when t-butyl alcohol is employed is presumably due partly to the low acidity of the alcohol but largely to steric effects.

*Experimental.—Hydrolyses of diphenyl terephthalate.* (*a*) To the ester (6·37 g.) in boiling ethanol (640 ml.) was added a solution of potassium hydroxide (1·1 g.) in ethanol (20 ml.), and the mixture was boiled under reflux for 1 hr. The acidic fraction separated from light petroleum in plates, m. p. 168—170°, and proved to be ethyl hydrogen terephthalate (Found: C, 61·9; H, 4·9. Calc. for $C_{10}H_{10}O_4$: C, 61·9; H, 5·2%) (lit.,[2] m. p. 168—170°).

(*b*) The ester (6·37 g.) and solid potassium hydroxide (1·0 g.) in boiling propan-2-ol (900 ml.) were boiled under reflux for 3 hr. The residue after removal of solvent was worked up in the usual way to give a neutral fraction (3·24 g.) which readily solidified. Recrystallisation from aqueous ethanol gave di-isopropyl terephthalate (2·7 g.) in leaflets, m. p. 54—55° (Found: C, 67·2; H, 7·4. Calc. for $C_{14}H_{18}O_4$: C, 67·2; H, 7·3%). The acidic fraction (1·27 g.) was taken up in boiling light petroleum (b. p. 60—80°) and filtered from a small amount of terephthalic acid. The monoisopropyl ester separated, on cooling, as needles, m. p. 167—169° (Found: C, 63·9; H, 5·9. Calc. for $C_{11}H_{12}O_4$: C, 63·5; H, 5·8%). Pfannl [3] records m. p. 55° and 166° for the di- and the mono-isopropyl ester, respectively.

(*c*) To the diphenyl ester (6·37 g.) in hot 2-ethoxyethanol (50 ml.) was added potassium hydroxide (1 g.) in water (5 ml.), and the mixture was boiled under reflux for 1½ hr. The neutral fraction (2·6 g.) did not crystallise at 0°. Distillation gave *bis-2-ethoxyethyl terephthalate*, b. p. 159—162°/0·2 mm., $n_D^{23}$ 1·4973 (Found: C, 61·9; H, 7·0. $C_{16}H_{22}O_6$ requires C, 61·9; H, 7·2%). The acidic fraction yielded *2-ethoxyethyl hydrogen terephthalate* (2·3 g., 48%) as plates, m. p. 93—94° [from benzene–light petroleum (b. p. 60—80°)] (Found: C, 60·8; H, 6·0. $C_{12}H_{14}O_5$ requires C, 60·5; H, 5·9%).

(*d*) To the diphenyl ester (6·37 g.) in boiling t-butyl alcohol (640 ml.) was added potassium hydroxide (1·5 g.) in water (20 ml.), and the mixture was boiled under reflux for 3 hr. The acidic fraction, on recrystallisation from aqueous alcohol, gave *phenyl hydrogen terephthalate*

[1] Hine and Hine, *J. Amer. Chem. Soc.*, 1952, **74**, 5266.
[2] Cohen and de Pennington, *J.*, 1918, **113**, 62.
[3] Pfannl. *Monatsh.*, 1911, **32**, 518.

(1·5 g., 31%) in plates, m. p. 238—240° (Found: C, 69·6; H, 4·2. $C_{14}H_{10}O_4$ requires C, 69·4; H, 4·2%).

(*e*) To the ester (6·37 g.) in phenol (64 g.) was added 2N-aqueous potassium hydroxide (10 ml.), and the mixture was heated on the steam-bath for 3 hr. After removal of the phenol under reduced pressure, the residue was extracted with hot water; the extract was filtered and acidified to give the monophenyl ester (2·2 g.), m. p. 230—235°, raised on recrystallisation from aqueous alcohol to 238—240°.

*Mono- and di-phenyl terephthalate from terephthaloyl chloride.* Terephthaloyl chloride (B.D.H. technical grade, 100 g.), phenol (120 g.), and pyridine (500 g.) were heated on the steam-bath for 1 hr., then poured on ice–water (2 kg.) with stirring. Solid sodium hydrogen carbonate (250 g.) was added portionwise, and the diphenyl ester (75 g., m. p. 190°) was filtered off and washed with water and with 50% ethanol (200 ml.). The combined filtrates were thoroughly extracted with chloroform, treated with charcoal, filtered, and acidified. The acidic material (35 g.) (partial melting at 230—240°) was extracted with ether (Soxhlet). Evaporation of the extract and recrystallisation of the residue from aqueous ethanol gave the monophenyl ester (22·9 g.), m. p. 238—240°, identical with that obtained in (*d*) and (*e*) above.

UNILEVER RESEARCH LABORATORY,
PORT SUNLIGHT, CHESHIRE.

[*Received, September 13th*, 1962.]

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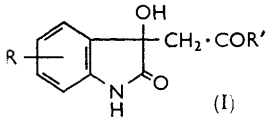
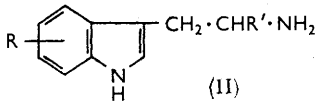
## 255. *A Novel Preparation of α-Substituted Tryptamines from Isatins.*

By C. S. FRANKLIN and A. C. WHITE.

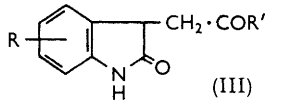
RECENT interest in the neuropharmacology of tryptamines, such as α-methyltryptamine (II; R = H, R′ = Me), led us to seek new methods for their preparation. Dioxindoles (I) were readily obtained by base-catalysed condensation of isatins with ketones.[1] Reduction of their oximes with lithium aluminium hydride gave the required tryptamines (II; seven examples), which probably arose by spontaneous dehydration of intermediate hydroxyindolines. α-Substituted tryptamines have also been prepared recently by reduction of the oximes of oxindoles (III) with sodium and ethanol;[2] and since our work was completed indoles have been prepared by reduction of 3-substituted oxindoles with lithium aluminium hydride in ether.[3]



(I)



(II)



(III)

The present reductions were also carried out with the sodium borohydride–aluminium chloride complex, which proved especially useful for the trifluoromethyl analogue (II; R = 7-$CF_3$, R′ = Me) since lithium aluminium hydride reduced the trifluoromethyl group to methyl. The reduction of oximes to amines with sodium borohydride–aluminium chloride has not apparently been reported before.

In preliminary experiments we used oxindole as a model compound for reduction and in our hands the only product isolated was indole. However, Smith and Yu [4] report that their reduction of this substance with lithium aluminium hydride gives indoline whereas Julian and Printy [5] were unable to reduce oxindole even at elevated temperatures.

[1] Elderfield, " Heterocyclic Compounds," New York, 1952, Vol. III, p. 222.
[2] Pietra and Tacconi, *Farmaco (Pavia)*, 1958, **13**, 893; 1961, **16**, 483, 492.
[3] Bettembourgh and David, *Bull. Soc. chim. France*, 1962, 772.
[4] Smith and Yu, *J. Amer. Chem. Soc.*, 1952, **74**, 1096.
[5] Julian and Printy, *J. Amer. Chem. Soc.*, 1949, **71**, 3206.

*Experimental.*—3-*Acetonyl*-3-*hydroxyoxindole* (I; R = H, R′ = Me). To a stirred suspension, at room temperature, of isatin (294 g., 2 mol.) in acetone (1 l.) was added diethylamine (100 ml.) in one portion. The solid dissolved exothermally during 30 min., to give a dark green solution. The mixture was stirred for a further 5½ hr. and the solid which separated was filtered off. The filtrate was evaporated to dryness on a steam-bath; the combined residues were triturated with water, collected, washed with cold acetone, and dried to give the dioxindole as a buff solid (350 g., 85%), m. p. 167—168° (decomp.) [Braude and Lindwall [6] give m. p. 167—168° (decomp.)].

In a similar manner the following were prepared: 3-*acetonyl*-3-*hydroxy*-7-*trifluoromethyloxindole* (I; R = 7-$CF_3$, R′ = Me), from 7-trifluoromethylisatin,[7] as pale yellow needles (43%) (from 50% aqueous ethanol), m. p. 199—201° (Found: C, 52·75; H, 3·7; N, 5·1; F, 20·2. $C_{12}H_{10}F_3NO_3$ requires C, 52·7; H, 3·7; N, 5·1; F, 20·9%), 3-acetonyl-3-hydroxy-5-methoxyoxindole (I; R = 5-OMe, R′ = Me) as yellow needles (40%), m. p. 176° (decomp.) [Pietra and Tacconi [2] give m. p. 171—172° (decomp.)], 3-*acetonyl*-3-*hydroxy*-7-*methyloxindole* (I; R = 7-Me, R′ = Me), from 7-methylisatin, as rhombs (51%) (from acetone), m. p. 201—202° (decomp.) (Found: C, 65·3; H, 5·8; N, 6·4. $C_{12}H_{15}NO_3$ requires C, 65·7; H, 6·0; N, 6·4%), 3-*acetonyl*-5-*fluoro*-3-*hydroxyoxindole* (I; R = 5-F, R′ = Me) (made by Miss L. Kruszynska), from 5-fluoroisatin,[8] as a yellow solid (64%) (from acetone), m. p. 147—149° (decomp.) (Found: C, 59·8; H, 4·55; N, 6·9. $C_{11}H_{10}FNO_3$ requires C, 59·2; H, 4·5; N, 6·3%), 3-hydroxy-3-phenacyloxindole (I; R = H, R′ = Ph), from isatin and acetophenone, as yellow needles (55%), m. p. 165° (decomp.) [Lindwall and Maclennan [8] give m. p. 169—172° (decomp.)], and 3-hydroxy-3-(3-methyl-2-oxobutyl)oxindole (I; R = H, R′ = $Pr^i$) (made by Dr. S. C. R. Meacock), from isatin and isopropyl methyl ketone as a cream powder (69%) (from benzene), m. p. 128—129° (Found: C, 66·5; H, 6·3; N, 6·5. Calc. for $C_{13}H_{15}NO_3$: C, 66·9; H, 6·5; N, 6·0%) (Pietra and Tacconi [2] report m. p. 138—139°).

3-*Hydroxy*-3-2′-*hydroxyiminopropyloxindole*. To 3-acetonyl-3-hydroxyoxindole (321 g., 1·6 moles) in hot 96% ethanol (2 l.) was added hydroxylamine hydrochloride (118 g., 1·7 moles) in water (1 l.) followed by sodium acetate (209 g., 2·6 moles) in water (1 l.). The solution was kept at room temperature for 1 hr., then evaporated to a small volume *in vacuo* on a water-bath. A solid separated which was filtered off and crystallised from water to give the *oxime* as needles (288 g., 82%), m. p. 179—180° (decomp.) (Found: C, 60·4; H, 5·5; N, 13·1. $C_{11}H_{12}N_2O_3$ requires C, 60·0; H, 5·5; N, 12·7%).

The same method gave analogous *oximes* containing also the following substituents: 7-*trifluoromethyl*, needles (72%) (from water), m. p. 99—102° (Found: N, 9·6. $C_{12}H_{11}F_3N_2O_3$ requires N, 9·7%), 5-*methoxy*-, pale yellow rhombs (77%) (from aqueous ethanol), m. p. 162—163° (Found: N, 11·0. $C_{12}H_{14}N_2O_4$ requires N, 11·2%), 5-*fluoro*-, cream needles (47%) (from aqueous methanol), m. p. 156·5—157° (decomp.) (Found: C, 55·2; H, 4·5; N, 11·1. $C_{11}H_{11}FN_2O_3$ requires C, 55·5; H, 4·7; N, 11·8%), and 7-*methyl* (83%), m. p. 200—201° (decomp.) (Found: C, 61·2; H, 6·1. $C_{12}H_{14}N_2O_3$ requires C, 61·5; H, 6·0%). 3-*Hydroxy*-3-(β-*hydroxyiminophenethyl*)*oxindole* formed needles (76%) (from ethanol), m. p. 203—204° (decomp.) (Found: C, 68·15; H, 5·2; N, 9·6. $C_{16}H_{14}N_2O_3$ requires C, 68·1; H, 5·0; N, 9·9%), and 3-*hydroxy*-3-(2-*hydroxyimino*-3-*methylbutyl*)*oxindole* (73%) (from benzene–methanol) had m. p. 139—140° (decomp.) (Found: C, 63·2; H, 6·25; N, 10·9. $C_{13}H_{16}N_2O_3$ requires C, 62·9; H, 6·5; N, 11·3%).

α-*Methyltryptamine* (II; R = H, R′ = Me). (*A*) 3-Hydroxy-3-2′-hydroxyiminopropyloxindole (10 g., 0·05 mol.) in tetrahydrofuran (250 ml.) was added dropwise to a stirred suspension, at room temperature, of lithium aluminium hydride (10 g., 0·26 mol.) in tetrahydrofuran (200 ml.): a vigorous reaction occurred. The red-brown mixture was refluxed for 12 hr., then cooled and treated with water (40 ml.), and the resulting suspension was filtered, evaporated to a small volume *in vacuo* on a water-bath, and extracted with ether. The organic phase was dried ($MgSO_4$) and distilled to afford the base (2·7 g., 34%), b. p. 137/0·3 mm. (bath 175°), giving a picrate, red-orange needles (from ethanol), m. p. and mixed m. p. 226°.

(*B*) To a stirred suspension of the oxime (44 g., 0·2 mol.) in freshly distilled bis-2-methoxyethyl ether (400 ml.), at room temperature, was added sodium borohydride (29·6 g., 0·8 mol.); an

[6] Braude and Lindwall, *J. Amer. Chem. Soc.*, 1933, **55**, 325.
[7] Maginnity and Gaulin, *J. Amer. Chem. Soc.*, 1951, **73**, 3579.
[8] Lindwall and Maclennan, *J. Amer. Chem. Soc.*, 1932, **54**, 4742.

exothermic reaction occurred and all the solid dissolved. When a solution of aluminium chloride (37·6 g.) in the ether (200 ml.) was added a complex separated. The mixture was heated at 100° for 48 hr., cooled, and filtered, and the residue was decomposed with 10N-sodium hydroxide and extracted with chloroform. Distillation of the extract yielded α-methyltryptamine (10·1 g., 29%).

The above mentioned oximes were reduced by one or other of the foregoing methods to give the following tryptamines: 5-*methoxy*-α-*methyl* (A) (45%), b. p. 187—190°/0·3 mm. [hydrochloride, plates (from ethyl acetate–methanol), m. p. and mixed m. p.[2] 112—113°], 7-methyl-α-methyl (A) (44%), b. p. 156—158°/0·2 mm., plates, m. p. 106—107°, 5-*fluoro*-α-*methyl* (A) (58%), b. p. 140—146°/0·5 mm. [hydrochloride, m. p. and mixed m. p.[2] 226—227° (decomp.)], α-phenyl (A) [hydrochloride pale orange needles, m. p.[2] 250—253° (decomp.)], α-*isopropyl* (A) [from benzene–light petroleum (b. p. 40—60°)], m. p. 108—110° (Found: C, 77·0; H, 9·0; N, 13·4. $C_{13}H_{18}N_2$ requires C, 77·2; H, 9·0; N, 13·85%), and α-*methyl*-7-*trifluoromethyl* (reaction time 1 hr.), b. p. 123—128°/0·2 mm., p$K_a$ 9·06 in 50% aqueous ethanol (Found: C, 59·4; H, 5·8; N, 11·4; F, 23·0. $C_{12}H_{13}F_3N_2$ requires C, 59·5; H, 5·4; N, 11·6; F, 23·5%).

*Reduction of oxindole.* To a stirred suspension of lithium aluminium hydride (6 g.) in ether (250 ml.) at room temperature was added oxindole (14 g.) in ether (1·5 l.). The mixture was refluxed for 10 hr., then cooled and decomposed with water (25 ml.). The resulting suspension was filtered and distilled, affording indole (2·55 g., 20%), b. p. 126°/15 mm. [1,3,5-trinitrobenzene adduct, yellow needles (from ethanol), m. p. and mixed m. p. 166—169°].

The authors thank Dr. R. E. Bowman for his advice and encouragement, Mr. C. A. Paterson for technical assistance, and Mr. F. H. Oliver for the microanalysis.

THE RESEARCH DEPARTMENT, PARKE, DAVIS & COMPANY,
HOUNSLOW, MIDDLESEX. [*Received, September* 19*th*, 1962.]

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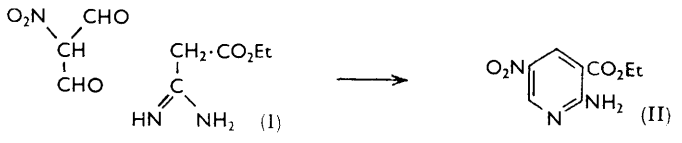
## 256. *A Synthesis, and Certain Properties, of Ethyl 2-Amino-5-nitronicotinate.*

By D. J. COLLINS.

DURING investigations of syntheses in the pyrimidine series, the amidino-ester (I) was treated with sodionitromalondialdehyde. Hale and Brill [1] reported that the interaction of sodionitromalondialdehyde and certain amidines gave 5-nitropyrimidines, and Dornow and Peterlein [2] that amidinoacetamide gave 2-aminonicotinamides with some dicarbonyl compounds.

It seemed possible that the condensation under examination might lead either to a pyrimidine or to a pyridine. However, it was found that ethyl 2-amino-5-nitronicotinate (II) was the sole product.




The identity of the ester (II) was established by its degradation to 2-amino-5-nitropyridine. Additionally, the derived acid gave 2-amino-3-bromo-5-nitropyridine when treated with bromine water.

The nicotinate (II) is almost immediately hydrolysed by warm aqueous alkali. On

[1] Hale and Brill, *J. Amer. Chem. Soc.*, 1912, **34**, 295.
[2] Dornow and Peterlein, *Chem. Ber.*, 1949, **82**, 257.

continued heating, the amino-group rapidly undergoes nucleophilic replacement, prolonged heating resulting in complete decomposition.

The 2-amino-group is acylated with difficulty and is not displaced by warm nitrosyl-sulphuric acid.

Simultaneous reduction of the nitro-group and the hydrolysis of the ester group occur when the nicotinate (II) is heated with anhydrous hydrazine, but reduction by ferrous hydroxide gives ethyl 2,5-diaminonicotinate in good yield.

*Experimental.—Ethyl amidinoacetate* (β-*amino*-β-*iminopropionate*) *hydrochloride.* Dry hydrogen chloride was passed into a mixture of dry ethyl cyanoacetate (145 g.), ethanol (57 g.), and ether (100 ml.) at 0° until the theoretical increase in weight (47 g.) occurred. Refrigeration overnight yielded white crystals, which on recrystallisation from acetone afforded ethyl ethoxycarbonylacetimidate hydrochloride (206 g.). This hydrochloride (25 g.) was shaken with 5N-ethanolic ammonia (25 ml.) for 2 hr., then concentrated under reduced pressure. On storage the liquid deposited a white solid and crystallisation of this from acetone gave *ethyl amidinoacetate hydrochloride* (5 g.) as needles, m. p. 104° (Found: C, 36·2; H, 7·0; Cl, 21·0; N, 16·4. $C_5H_{11}ClN_2O_2$ requires C, 36·0; H, 6·7; Cl, 21·3; N, 16·8%).

*Ethyl* 2-*amino*-5-*nitronicotinate.* (*a*) Ethyl amidinoacetate hydrochloride (1 g.) was added to a solution of sodionitromalondialdehyde (1 g.) in water (10 ml.). On the addition of a few drops of piperidine, an orange precipitate was immediately formed, crystallisation of which from acetic acid gave *ethyl* 2-*amino*-5-*nitronicotinate* (1·1 g.) as pale yellow needles, m. p. 196° (Found: C, 45·9; H, 4·5; N, 20·1. $C_8H_9N_3O_4$ requires C, 45·5; H, 4·3; N, 19·9%).

(*b*) Ethyl ethoxycarbonylacetimidate hydrochloride (75 g.) in ethanol (100 ml.) was stirred in 5N-ethanolic ammonia (150 ml.) for 1 hr. Sodionitromalondialdehyde (50 g.) in water (500 ml.) containing piperidine (5 ml.) was gradually added. Crystallisation of the precipitate gave 52 g. of ethyl 2-amino-5-nitronicotinate.

The *acetyl derivative*, prepared by refluxing the ester in acetic anhydride for 1 hr., recrystallised from ethanol as needles, m. p. 117° (Found: C, 47·3; H, 4·6; N, 16·7. $C_{10}H_{11}N_3O_5$ requires C, 47·7; H, 4·4; N, 16·6%). The *benzoyl derivative* was obtained by refluxing the ester with benzoyl chloride for ½ hr. Addition of the mixture to sodium carbonate solution and crystallisation of the precipitate from ethanol gave the benzoyl derivative as pale yellow needles, m. p. 143° (Found: C, 57·0; H, 4·4; N, 13·0. $C_{15}H_{13}N_3O_5$ requires C, 57·2; H, 4·2; N, 13·3%).

*Hydrolysis of ethyl* 2-*amino*-5-*nitronicotinate.* (*a*) 5% Alcoholic potassium hydroxide (10 ml.) was added to a boiling solution of the ester (1 g.) in ethanol (150 ml.). Almost immediately, potassium 2-amino-5-nitronicotinate separated as yellow needles. Acidification of an aqueous solution of the potassium salt to pH 3 afforded 2-amino-5-nitronicotinic acid as a pale yellow powder, insoluble in common neutral solvents, m. p. 240° (decomp.) (lit.,[3] 233°) (Found: C, 39·5; H, 3·0; N, 23·1. Calc. for $C_6H_5N_3O_4$: C, 39·4; H, 2·8; N, 23·0%).

(*b*) The ester (1 g.) was heated in 25% aqueous potassium hydroxide (10 ml.) for 15 min. After cooling, the solution was adjusted to pH 3. A small amount of 2-hydroxy-5-nitronicotinic acid, m. p. 265° (lit.,[3] 265°), separated (Found: C, 39·5; H, 2·2; N, 15·6. Calc. for $C_6H_4N_2O_5$: C, 39·2; H, 2·2; N, 15·2%).

(*c*) The ester (20 g.) was boiled under reflux with 50% sulphuric acid for ½ hr. On cooling and dilution of the mixture with an equal volume of water, plates of 2-*amino*-5-*nitronicotinic acid sulphate* (20·5 g.), m. p. 185° (decomp.), separated (Found: S, 11·6. $C_6H_7N_3O_8S$ requires S, 11·4%).

2-*Amino*-5-*nitropyridine.* The preceding sulphate (5 g.) was heated in boiling cyclohexanone (125 ml.) for 5 min. On cooling, a solid separated. Crystallisation from dilute aqueous ammonia gave 2-amino-5-nitropyridine (2·3 g.), m. p. and mixed m. p. 188°.

2-*Amino*-3-*bromo*-5-*nitropyridine.* Potassium 2-amino-5-nitronicotinate (1 g.) in water (50 ml.) was slowly added, with stirring, to a solution of bromine (1 g.) in 10% sulphuric acid (50 ml.) at 50°. 2-Amino-3-bromo-5-nitropyridine separated as pale yellow needles, and recrystallised from acetic acid as pale yellow plates, m. p. and mixed m. p. 222° [lit.,[4] 215° (decomp.)].

[3] Rath, *Annalen*, 1931, **486**, 284.
[4] Tschitschibabin, *J. Russ. Phys. Chem. Soc.*, 1918—1920, **50**, 492.

*Reaction of the ester with hydrazine.* Anhydrous hydrazine (2 ml.) and ethyl 2-amino-5-nitronicotinate (1 g.) were boiled in absolute ethanol (150 ml.) for 8 hr. On cooling, black needles of *hydrazinium 2,5-diaminonicotinate* (0·7 g.) separated (Found: N, 38·2. $C_6H_{11}N_5O_2$ requires N, 37·8%). Acidification of an aqueous solution of this salt with acetic acid gave a yellow precipitate. Recrystallisation of this from water yielded *2,5-diaminonicotinic acid* as plates, m. p. 302° (decomp.) (Found: C, 47·3; H, 4·4; N, 27·7. $C_6H_7N_3O_2$ requires C, 47·0; H, 4·6; N, 27·4%), sparingly soluble in water to an orange solution which became yellow on acidification and deep purple on addition of alkali hydroxide.

*Ethyl 2,5-diaminonicotinate.* Freshly precipitated ferrous hydroxide [from ferrous sulphate heptahydrate (12·9 g.) in water (50 ml.) and barium hydroxide octahydrate (14·65 g.) in water (50 ml.)] and ethyl 2-amino-5-nitronicotinate (1 g.) were boiled for ½ hr., then filtered. The filtrate and washings were evaporated to 5 ml. and saturated with sodium carbonate; a dark red oil separated that was extracted in benzene. The benzene layer was evaporated to 2 ml. and, on cooling, *ethyl 2,5-diaminonicotinate* (0·7 g.) separated as yellow rods, m. p. 93° (from benzene) (Found: C, 52·7; H, 6·25; N, 22·8. $C_8H_{11}N_3O_2$ requires C, 53·0; H, 6·1; N, 23·2%).

Normal diazotisation of the diamino-ester and coupling gave *ethyl 2-amino-5-2′-naphthylazonicotinate*, crystallising from acetic acid as dark red plates, m. p. 225° (Found: C, 64·4; H, 4·9; N, 15·9. $C_{18}H_{16}N_4O_3$ requires C, 64·3; H, 4·8; N, 16·6%).

*Ethyl 2,5-dibenzamidonicotinate* slowly separated from a solution of the ester in pyridine, to which benzoyl chloride had been added. It crystallised from ethanol as buff needles, m. p. 172° (Found: C, 67·3; H, 4·7; N, 11·2. $C_{22}H_{19}N_3O_4$ requires C, 67·8; H, 4·9; N, 10·8%). *Ethyl 2-amino-5-acetamidonicotinate* separated as matted white needles when the ester, in benzene, was warmed with acetic anhydride. On recrystallisation from benzene, it had m. p. 192° (Found: C, 53·85; H, 6·2; N, 18·4. $C_{10}H_{13}N_3O_3$ requires C, 53·8; H, 5·9; N, 18·8%) and dissolved in ethanol, benzene, etc., to colourless solutions having a blue fluorescence.

BOURNEMOUTH MUNICIPAL COLLEGE OF TECHNOLOGY AND COMMERCE.

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## 257. *The Synthesis of* p-*Vinylbenzoic Acid.*

By P. JÄGER and E. S. WAIGHT.

A SAMPLE of *p*-vinylbenzoic acid was required in connection with an investigation into the γ-irradiation of some crystalline derivatives of styrene.[1] Multi-stage routes giving the acid in low overall yields have been reported by several groups of workers.[2] The convenient four-stage synthesis by Bissell and Spenger [3] gave a product which, judged from its melting point (123—128°), seems not to have been pure. A three-stage synthesis from polystyrene [4] suffers from an inefficient thermal depolymerization and gives the acid in an overall yield of only 18%. We found it convenient to prepare *p*-vinylbenzoic acid by dehydrobromination of *p*-2-bromoethylbenzoic acid, the preparation of which in high yield has been described by Foreman and McElvain.[5] By this route the acid can be obtained in three steps from phenethyl bromide in better than 50% yield.

*Experimental.*—p-2-*Bromoethylbenzoic acid.* Phenethyl bromide (L. Light and Co. Ltd.) was converted in 85% yield (lit., 83%) into 4-2′-bromoethylacetophenone, b. p. 134—137°/

[1] P. Jäger, Ph.D. Thesis, London, 1961.
[2] Marvel and Overberger, *J. Amer. Chem. Soc.*, 1945, **67**, 2250; Bachman, Carlson, and Robinson, *ibid.*, 1951, **73**, 1964; Cazes, *Compt. rend.*, 1958, **247**, 1874; Leebrick and Ramsden, *J. Org. Chem.*, 1958, **23**, 953; Kolesnikov and Soboleva, *Bull. Acad. Sci. U.S.S.R.*, 1958, 733; Dyksterhuis and Rivett, *J.S. African Chem. Inst.*, 1960, **13**, 68.
[3] Bissell and Spenger, *J. Org. Chem.*, 1959, **24**, 1146.
[4] Merrill, *J. Org. Chem.*, 1961, **26**, 1301.
[5] Foreman and McElvain, *J. Amer. Chem. Soc.*, 1940, **62**, 1435.

1 mm., $n_D^{19}$ 1·5742, and this then oxidised to *p*-2-bromoethylbenzoic acid (7.1%, lit., 87%), m. p. 209—210° (lit., 205—207°), both steps being carried out as described by Foreman and McElvain.[5]

p-*Vinylbenzoic acid.* A suspension of *p*-2-bromoethylbenzoic acid (7·5 g.), potassium hydroxide (8 g.), and quinol (50 mg.) in ethanol (35 ml.) was heated under reflux for 1 hr. The mixture was cooled, and the solid removed by filtration, washed with cold (0°) water (10 ml.), and dissolved in cold (20°) water (50 ml.). The solution was acidified with concentrated hydrochloric acid, and the precipitated acid removed by filtration, washed with cold (0°) water (10 ml.), and dried *in vacuo*. The pure acid (4·15 g.) crystallized in plates (from aqueous alcohol), m. p. 140° (lit.,[2] 136° to 143—144°), $\lambda_{max.}$ (in EtOH) 213 (ε 10,800), 266 (ε 22,200), $\lambda_{infl}$ 295 mμ (ε 1020), $\nu_{max.}$ (in $CCl_4$) 1745w, 1701s, 1613m, 1422s, 1319m, 1290s, 1220w, 1186m, 1131w, 1115w, 1083w, 1018w, 988m, 920m, 863m cm.$^{-1}$.

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CHEMISTRY DEPARTMENT,
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
S. KENSINGTON, LONDON, S.W.7. [*Received, September 20th,* 1962.]

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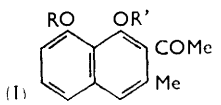
## 258. 2-*Acetyl*-3-*methylnaphthalene*-1,8-*diol and its* 8-*Glucoside, Constituents of the Broad-leaved Dock,* Rumex obtusifolius.

By R. E. BOWMAN, C. P. FALSHAW, C. S. FRANKLIN, A. W. JOHNSON, and T. J. KING.

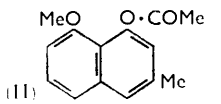
IT has been shown by Brittain and Collier [1] that saline extracts prepared from broad-leaved dock (*Rumex obtusifolius*) are antagonistic to acetylcholine, histamine, and 5-hydroxytryptamine, substances which have been shown [2] to occur in the sting of the common nettle (*Urtica dioca* L.). We have investigated the components of an ethanolic extract of dock leaves and by chromatography on alumina of the water-soluble part of the extract we have isolated a crystalline glycoside in a yield of 0·07% (based on undried leaves). The glycoside, $C_{19}H_{22}O_8$, contained no *O*-methyl groups, and a strong band in its infrared spectrum at 1661 cm.$^{-1}$ suggested the presence of a carbonyl group probably conjugated with an aromatic ring. Acid hydrolysis of the glycoside yielded glucose (identified by paper chromatography in two solvent systems). The aglycone was a pale yellow crystalline compound, $C_{13}H_{12}O_3$, which gave a diacetate and a dibenzoate. It was present in small amount in the leaves but could be isolated more conveniently by extraction of dock roots. The composition and properties of the aglycone and its derivatives suggested that it might be 2-acetyl-3-methylnaphthalene-1,8-diol [3] (musizin) (I; R = R′ = H), previously isolated from *Malopsis eminii*, and this was confirmed by direct comparisons (we are indebted to Dr. J. W. W. Morgan for supplying the authentic samples). Methylation of our glycoside with diazomethane gave a gum, which by hydrolysis afforded a small yield of 2-acetyl-8-hydroxy-1-methoxy-3-methylnaphthalene (I; R = H, R′ = Me), thus establishing the structure of the glycoside as (I; R = glucosidyl, R′ = H). A number of 2-acylnaphthalene-1,8-diols have been isolated recently from plant sources. Thus the 8-rutinoside corresponding to our glucoside has been isolated by Cooke and his

[1] Brittain and Collier, *J. Physiol.*, 1956, **135**, 58P.
[2] Emmelin and Feldburg, *J. Physiol.*, 1947, **106**, 490; Collier and Chesher, *Brit. J. Pharmacol.*, 1956, **11**, 186.
[3] Cavell, King, and Morgan, *J.*, 1961, 702.

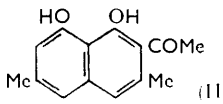
colleagues [4] from *Dianella laevis* and 2-acetylnaphthalene-1,8-diol from *Rhammus frangula*.[5] Further, nepodin [6] from *Rumex nepalensis* is probably also a 2(or 7)-acylnaphthalene-1,8-diol. Musizin has recently been synthesised [7] by a lengthy route from *m*-methoxybenzaldehyde but, before the appearance of this Note, we had obtained musizin from 1-acetoxy-8-methoxy-3-methylnaphthalene (II) by a Fries rearrangement which also caused demethylation of the 8-methoxy-group. We thank Professor W. B. Whalley for supplying us with details of the preparation of 1-hydroxy-8-methoxy-3-methylnaphthalene before their publication.



(I)



(II)



(III)

The 2-acylnaphthalene-1,8-diols almost certainly arise biogenetically from self-condensation of acetate units and indeed Collie [8] showed that self-condensation of acetylacetone in presence of piperidine gave 2-acetyl-3,6-dimethylnaphthalene-1,8-diol (III).

*Experimental.*—M. p.s were determined on the Kofler block; ultraviolet absorptions were measured for ethanol solutions with a Unicam S.P. 700 instrument; alumina was Spence's grade H; and light petroleum was the fraction of b. p. 60—80°.

*Extraction of dock leaves.* Freshly collected leaves (1·5 kg.) were disintegrated with ethanol (4 l.) and filtered. The residue was again extracted with ethanol (4 l.), and the combined extracts were evaporated in a vacuum. The gummy residue (89 g.) was dissolved in 50% aqueous methanol (700 c.c.) and extracted with light petroleum (6 × 200 c.c.). The methanolic layer was then evaporated and this residue was extracted with water (300 c.c.). The aqueous extract was evaporated to dryness to a residue that was taken up in 90% ethanol (300 c.c.). The filtered solution was chromatographed on alumina to give fractions: A, from the first 5 l. of 90% ethanol, a green band; B, from the next 4 l. of 90% ethanol, a yellow band with a strong blue-green fluorescence in ultraviolet light; C, eluted with 4 l. of 80% ethanol; D, eluted with 4 l. of 70% ethanol. Fractions, B, C, and D were similar in appearance and were evaporated *in vacuo* to give a residue which crystallised from water–ethanol (3 : 1) to give the *glycoside* (1·0 g.) as colourless needles, m. p. 203—204°, $[\alpha]_D^{25}$ (in EtOH) −119° (Found: C, 60·5; H, 5·9. $C_{19}H_{22}O_8$ requires C, 60·3; H, 5·9%), $\lambda_{max.}$ 225 (ε 40,000), 301 (ε 4600) and 338 mμ (ε 4400).

In another experiment, the light petroleum extract (from 5·1 kg. of dock leaves) was washed with aqueous sodium carbonate. Acidification of this extract gave musizin (205 mg.) which crystallised from light petroleum as yellow needles, m. p. 164—165° alone or mixed with an authentic specimen.

*Isolation of the aglycone.* (*a*) Fresh roots (2·7 kg.) of *Rumex obtusifolius* were minced with methanol (4 l.). The extract was collected by filtration and the residue was stirred overnight with methanol (4 l.). The combined extracts were evaporated *in vacuo* to 4 l. and then extracted with light petroleum (6 × 500 c.c. and 2 × 300 c.c.). The light petroleum extracts were combined and extracted with 10% aqueous sodium carbonate (2 × 400 c.c.). The carbonate extract was acidified and the precipitate was chromatographed in acetone solution on magnesium oxide (400 g.). Acetone eluted a yellow band which was rechromatographed on a smaller magnesia column. The eluate was then evaporated and the residue crystallised from light petroleum, to give 2-acetyl-3-methylnaphthalene-1,8-diol (159 mg.), m. p. 153—162°, raised to 164—165° by sublimation (Found: C, 72·3; H, 5·4. Calc. for $C_{13}H_{12}O_3$: C, 72·2; H, 5·6%), $\lambda_{max.}$ 225 (ε 35,000), 262 (ε 19,000), 303 (ε 6200), 345 (ε 6300) and 403 mμ (ε 2800). The

[4] Batterham, Cooke, Duewell, and Sparrow, *Austral. J. Chem.*, 1961, **14**, 637.
[5] Pailer, Jentzsch, Kump, and Fuchs, *Monatsh.*, 1958, **89**, 540.
[6] Murakami and Matsushima, *Chem. and Pharm. Bull.* (*Japan*), 1961, **9**, 641.
[7] Harri, Hanaoka, and Tamura, *Chem. and Ind.*, 1962, 1243.
[8] Collie, *J.*, 1893, **63**, 329; 1907, **91**, 1806; see also Birch, Cameron, and Richards, *J.*, 1960, 4395; Bethell and Maitland, *J.*, 1962, 3751.

m. p. was undepressed on admixture with an authentic sample of musizin and the infrared spectra were identical. The diacetate had m. p. 187—188° undepressed by musizin diacetate (m. p. 189—190°), and the dibenzoate had m. p. 187—188° undepressed by musizin dibenzoate (m. p. 187—188°).

(*b*) A suspension of the glycoside (100 mg.) in 2N-hydrochloric acid (30 c.c.) was boiled for 30 min. The solution was then cooled to 0° and the pale yellow powder which separated crystallised from light petroleum, giving musizin, m. p. 158—162°, raised to 164—165° by sublimation at 120°/0·01 mm. The filtrate, after removal of musizin, was examined by paper chromatography on Whatman no. 1 paper with butan-1-ol–acetic acid–water (4 : 1 : 5) and propan-2-ol–pyridine–acetic acid–water (8 : 8 : 1 : 4). Spots at $R_F$ 0·2 (first system) and 0·65 (second system) revealed the presence of glucose. No separation was achieved when the sample was mixed with authentic glucose and subjected to chromatography as above.

*Hydrolysis of the methylated glucoside.* The glucoside (70 mg.) in methanol (50 c.c.) was treated with an excess of ethereal diazomethane at room temperature for 3 hr. Removal of the solvents left a colourless gum which was heated to the b. p. in suspension in 2N-hydrochloric acid for 30 min. Ether-extraction of the cooled solution gave a yellow gum which was sublimed twice at 70—80°/0·1 mm. to give 7-acetyl-8-methoxy-6-methyl-1-naphthol, m. p. 74—75°, undepressed by an authentic specimen.[3] The infrared spectra of the two samples were also identical.

1-*Acetoxy*-8-*methoxy*-3-*methylnaphthalene*. 8-Methoxy-3-methyl-1-naphthol [9] (5 g.) was treated with acetic anhydride in presence of pyridine at 100° for 1 hr. After crystallisation from ethanol, the *acetoxy-compound* (2·5 g.) formed needles, m. p. 142—144° (Found: C, 72·9; H, 5·9. $C_{14}H_{14}O_3$ requires C, 73·0; H, 6·1%), $\lambda_{max.}$ 224, 297, 314, and 328 mμ (ε 977,000, 6600, 4900, and 4360, respectively).

2-*Acetyl*-3-*methylnaphthalene*-1,8-*diol* (*musizin*). The acetate (1·54 g.) from the previous experiment was heated with aluminium chloride (1·8 g.) at 130—140° during 3 hr. After cooling, 10% hydrochloric acid (200 c.c.) was added; a red precipitate separated. The mixture was heated to the b. p., the red precipitate becoming yellow. The solution was then cooled and extracted with ether (4 × 100 c.c.; 3 × 50 c.c.). The combined ethereal extracts were washed with water and then with 5% aqueous sodium carbonate (4 × 100 c.c.). Acidification of the combined aqueous sodium carbonate extracts gave a yellow precipitate which was separated and dried. It was extracted with hot light petroleum (2 × 100 c.c.; 1 × 50 c.c.), and concentration of the extract gave musizin as yellow needles (150 mg.), m. p. 164—165°, undepressed on admixture with the natural product (Found: C, 72·3; H, 5·45. Calc. for $C_{13}H_{12}O_3$: C, 72·2; H, 5·6%). The infrared spectra (in $CCl_4$) of the natural and the synthetic product were superimposable.

We thank Dr. Collier for suggesting this problem.

PARKE DAVIS LTD., HOUNSLOW, MIDDLESEX.
THE UNIVERSITY, NOTTINGHAM.

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[9] Professor W. B. Whalley, personal communication.

## 259. *Some Complexes of Tertiary Phosphines and Tertiary Diphosphines with Titanium Chlorides.*

By J. Chatt and R. G. Hayter.

Chatt, Hart, and Watson [1] recently reported a series of complexes of ditertiary phosphines with the zero-valent metals vanadium, chromium, iron, cobalt, and nickel of the first transition series. In an unsuccessful attempt to extend this series to titanium, we obtained a number of brightly coloured complexes of tertiary phosphines with titanium tetrachloride as listed in the Table.

The compounds were prepared by mixing solutions of titanium tetrachloride and the phosphine ligands in " boiled out " benzene or light petroleum under nitrogen in rigorously dry conditions. No evidence of any further reaction with an excess of the ligand was observed and the compounds obtained were extremely sensitive to moisture. A typical preparation follows.

*Tetrachlorobis(triphenylphosphine)titanium*(IV). A solution of titanium tetrachloride (1·75 g.) in benzene (15 c.c.) was slowly added to a solution of triphenylphosphine (4·85 g.) in benzene (15 c.c.) to give a dark red solution and a precipitate. The precipitate was filtered off, washed with benzene and light petroleum (b. p. 60—80°), and recrystallised from benzene–light petroleum (b. p. 60—80°).

The *bipyridyl analogue* of the compounds (I—V), namely [$TiCl_4$bipy], was obtained as a pale yellow precipitate from carbon tetrachloride solutions of the reactants. It did not melt at under 300° (Found: C, 35·1; H, 2·5; Cl, 40·0; N, 8·1. $C_{10}H_8Cl_4N_2Ti$ requires C, 34·8; H, 2·3; Cl, 40·95; N, 8·1%).

No molecular weight or other physical constants of these compounds was obtained because of their extreme sensitivity to moisture, but it is unlikely that the *compounds* (I—V) can be other than octahedrally co-ordinated unimolecular non-ionic complexes.

*Compound* (VI) was prepared in low yield by dissolving titanium trichloride as fine powder in a boiling solution of the phosphine in benzene under reflux.

| | Compound | M. p. (vac.) | Colour | Crystn. solvent * | Found (%) C | Found (%) H | Formula | Reqd. (%) C | Reqd. (%) H |
|---|---|---|---|---|---|---|---|---|---|
| (I) | $[TiCl_4(PEt_3)_2]$ | 144·5—148·0° | Dark red | $C_6H_6$–Pet | 33·7 | 7·1 | $C_{12}H_{30}Cl_4P_2Ti$ | 33·8 | 7·1 |
| (II) | $[TiCl_4(PPh_3)_2]$ | 151·5—153·0 | Dark red | $C_6H_6$–Pet | 60·3 | 4·3 | $C_{36}H_{30}Cl_4P_2Ti$ | 60·5 | 4·2 |
| (III) | $[TiCl_4\{C_2H_4(PEt_2)_2\}]$ | 214—219 | Red | $C_6H_6$–Pet | 30·35 | 6·3 | $C_{10}H_{24}Cl_4P_2Ti$ | 30·3 | 6·1 |
| (IV) | $[TiCl_4\{C_2H_4(PMe_2)_2\}]$ | 281—285 | Orange | $C_6H_6$ | 21·2 | 5·0 | $C_6H_{16}Cl_4P_2Ti$ | 21·2 | 4·75 |
| (V) | $[TiCl_4\{o\text{-}C_6H_4(PEt_2)_2\}]$ | 256·5—259·0 | Red | $C_6H_6$–Pet | 37·6 | 5·6 | $C_{14}H_{24}Cl_4P_2Ti$ | 37·9 | 5·45 |
| (VI) | $TiCl_3\{C_2H_4(PEt_2)_2\}$ | 312—319 | Dark brown | $C_6H_6$ | 32·9 | 6·9 | $C_{10}H_{24}Cl_3P_2Ti$ | 33·3 | 6·9 |

* Pet = light petroleum.

Imperial Chemical Industries Limited, Heavy Organic Chemicals Division,
Akers Research Laboratories,
The Frythe, Welwyn, Herts.

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[1] Chatt and Watson, *J.*, 1962, 2545, and references therein.