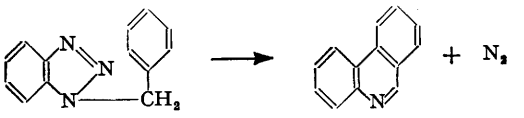
NOTES.

222. *The Pyrolysis of 1-Benzylbenzotriazole and Some Homologues thereof.*

By M. S. GIBSON.

THE Graebe–Ullmann synthesis of carbazoles from 1-phenylbenzotriazoles by pyrolysis indicated that the thermal decomposition of 1-benzylbenzotriazole and its derivatives might provide a convenient route to phenanthridines :



1-Benzylbenzotriazole, prepared by a modification of the method of Krollpfeiffer, Pötz, and Rosenburg,[1] was found to be very stable to pyrolysis. Slow decomposition occurred at 350—400°, or in phosphoric acid solution [2] at 220°, but gave only indefinite or carbonaceous material. When, however, the triazole was heated with a little copper powder at 350—400° under nitrogen, phenanthridine was isolated in small yield as picrate, together with (probably) toluene.

Alkylation of benzotriazole with 2- and 4-methylbenzyl chloride gave respectively 1-2′- and 1-4′-methylbenzylbenzotriazole; these have the expected ultraviolet absorptions.[1] Pyrolysis gave 8- and 6-methylphenanthridine, together with (probably) *o*- and *p*-xylene, respectively.

As an alternative route to the 1-benzylbenzotriazoles, *o*-chloronitrobenzene was condensed with benzylamine by a modification of Kehrmann and Tichvinsky's method.[3] Reduction to the diamine, followed by treatment with nitrous acid, afforded 1-benzylbenzotriazole, together with a large amount of tar. An attempt to prepare 1-2′-methylbenzylbenzotriazole by analogous reactions failed.

Experimental.—*1-Benzylbenzotriazole.* A hot solution of benzotriazole (5 g.) in ethanol (18 c.c.) was added to sodium ethoxide (from sodium, 1 g.) in ethanol (14 c.c.) on the steam-bath. After 5 min., benzyl chloride (5·4 g.) in ethanol (8 c.c.) was added, and the mixture was heated on the steam-bath for 3 hr. The precipitated sodium chloride was removed, and the filtrate evaporated. Crystallisation of the residue from methanol afforded 1-benzylbenzotriazole as prisms, m. p. 115—116°. Krollpfeiffer *et al.*[1] give m. p. 115—116°.

Pyrolysis. 1-Benzylbenzotriazole (4 g.) with a trace of copper powder was heated at 350—400° under nitrogen. Small quantities of volatile material were allowed to escape from time

[1] Krollpfeiffer, Pötz, and Rosenburg, *Ber.*, 1938, **71**, 596.
[2] Robinson and Thornley, *J.*, 1924, 2169.
[3] Kehrmann and Tichvinsky, *Annalen*, 1896, **290**, 293.

to time. The reaction was judged to be complete when no more volatile material was formed (5—6 hr.). The dark product was extracted with hot dilute hydrochloric acid (charcoal), and picric acid was added to the filtrate. The precipitated phenanthridine picrate formed yellow needles (from water), m. p. and mixed m. p. 244—245° (Found: C, 56·2; H, 3·0. Calc. for $C_{19}H_{12}O_7N_4$: C, 55·9; H, 2·9%). 9 : 10-Dihydrophenanthridine [4] gave a picrate, red needles (from ethanol), m. p. 238° (Ritchie [5] gives m. p. 238°), depressed to 218—223° (decomp.) on admixture with the foregoing picrate.

1-2′-*Methylbenzylbenzotriazole.* Benzotriazole (10 g.) was alkylated with 2-methylbenzyl chloride [6] (12 g.), as in the previous case. From methanol, 1-2′-*methylbenzylbenzotriazole* (15 g.) separated as cubes, m. p. 84—85° (Found: C, 75·7; H, 5·8; N, 18·8. $C_{14}H_{13}N_3$ requires C, 75·3; H, 5·8; N, 18·9%).

8-*Methylphenanthridine picrate.* The foregoing triazole (10 g.), pyrolysed as above, gave an orange-brown oil, b. p. 170—270°/17 mm., which was dissolved in ether and extracted with dilute hydrochloric acid. The acid extract (charcoal) was basified and extracted with ether. Addition of picric acid to the dried ethereal solution precipitated 8-*methylphenanthridine picrate* (400 mg.), which crystallised from water in yellow needles, m. p. 253—254° (Found: C, 56·7; H, 3·5; N, 13·0. $C_{20}H_{14}O_7N_4$ requires C, 56·9; H, 3·3; N, 13·3%).

The volatile material (1 g.) collected during the pyrolysis was distilled, and a fraction (650 mg.), b. p. 142—146°, smelling of *o*-xylene was collected. This was oxidised by means of potassium permanganate and sodium hydroxide solutions to phthalic acid, m. p. 190—200° (anhydride, m. p. and mixed m. p. 128—129°).

6-*Methylphenanthridine picrate.* Benzotriazole (10 g.) and 4-methylbenzyl chloride [7] (12 g.) similarly yielded 1-4′-*methylbenzylbenzotriazole* (14 g.), needles (from methanol), m. p. 106—107° (Found: C, 75·4; H, 5·9%). Treated as above, this triazole (10 g.) gave 6-*methylphenanthridine picrate* (350 mg.), yellow needles (from water), m. p. 245—246° (Found: C, 57·3; H, 3·6; N, 13·0%).

Redistillation of the volatile material (900 mg.) evolved during the pyrolysis afforded a fraction (500 mg.), b. p. 140—145°, smelling of *p*-xylene; this was oxidised as in the previous case and the resulting terephthalic acid converted by way of the chloride into the dimethyl ester, needles (from methanol), m. p. and mixed m. p. 139—140°.

N-o-*Nitrophenylbenzylamine.* The following modification of the known method [8] gave an enhanced yield. A stirred mixture of *o*-chloronitrobenzene (16 g.), benzylamine (10·5 g.), and anhydrous potassium carbonate (7 g.) was heated at 150° for 2 hr., then cooled, powdered, and extracted with boiling ethanol. The concentrated extract deposited the amine (18 g.) as orange prisms, m. p. 74—75°. Kehrmann and Messinger [8] record m. p. 74—75°.

A solution of stannous chloride (65 g.) in concentrated hydrochloric acid (200 c.c.) at 100° was cautiously added to one of this amine (16 g.) in boiling acetic acid. An excess of sodium hydroxide solution was added to the cooled mixture, and the precipitated solid was collected and extracted with boiling ethanol. The filtrate was also washed with ether, the extract being concentrated and the residue added to the ethanolic extract already obtained. Water (80 c.c.) and concentrated hydrochloric acid (100 c.c.) were added to the ethanolic solution, and, after cooling to 0—5°, a solution of sodium nitrite (6 g.) in water (12 c.c.) was added with stirring. An intense red colour developed, and much tar separated. The mixture was rendered slightly alkaline by 5% sodium hydroxide solution. The dark semi-solid material was collected and washed with water; four crystallisations from aqueous methanol (charcoal) afforded 1-benzylbenzotriazole (1 g.) as pale buff prisms, m. p. and mixed m. p. 115—116°.

2-*Methyl*-N-o-*nitrophenylbenzylamine.* 2-Methylbenzylamine (15 g.), b. p. 80—82°/15 mm., was prepared by hydrogenation of *o*-tolunitrile (20 g.) in ethanol (120 c.c., saturated with ammonia at 0°) with Raney nickel at 100°/120 atm. Under analogous conditions, *p*-tolunitrile (20 g.) gave 4-methylbenzylamine (16 g.), b. p. 82—83°/15 mm. Hydrogenolysis of *N*-benzyl linkages appeared to be comparatively slow under these conditions.

Condensation of *o*-chloronitrobenzene (16 g.) with 2-methylbenzylamine (12 g.) in presence of potassium carbonate (7 g.) was effected at 160—165° (2 hr.). Isolated as in the earlier case, 2-*methyl*-N-o-*nitrophenylbenzylamine* (18 g.) separated from ethanol in orange prisms, m. p. 103—104° (Found: C, 69·6; H, 5·9; N, 11·6. $C_{14}H_{14}O_2N_2$ requires C, 69·4; H, 5·8; N, 11·6%).

[4] Wooten and McKee, *J. Amer. Chem. Soc.*, 1949, **71**, 2946.
[5] Ritchie, *J. Proc. Roy. Soc. New South Wales*, 1945, **78**, 177.
[6] Smith and Spillane, *J. Amer. Chem. Soc.*, 1940, **62**, 2639.
[7] Blanc, *Bull. Soc. chim. France*, 1923, **33**, 313.
[8] Kehrmann and Messinger, *J. prakt. Chem.*, 1892, **46**, 565.

The *acetyl derivative* crystallised from aqueous ethanol in colourless plates, m. p. 124—125° (Found: C, 67·7; H, 5·7; N, 9·8. $C_{16}H_{16}O_3N_2$ requires C, 67·6; H, 5·6; N, 9·9%).

The author is grateful to Professor Sir Robert Robinson, F.R.S., for advice, to Dr. E. A. Braude for a gift of phenanthridine, and to the Department of Scientific and Industrial Research for a maintenance grant.

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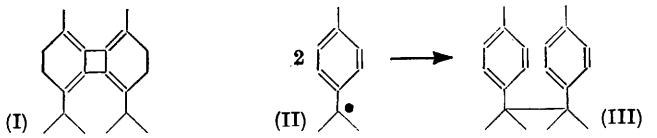
223. *Structure of a By-product in the Formation of Ascaridole Glycol Anhydride.*

By A. H. BECKETT and G. O. JOLLIFFE.

IN the preparation of ascaridole glycol anhydride by dropwise addition of ascaridole to boiling *p*-cymene, Thoms and Dobke [1] reported the presence of a crystalline by-product, $C_{20}H_{28}$, m. p. 158°, to which they tentatively assigned formula (I). Under similar conditions we obtained a compound, $C_{20}H_{26}$, m. p. 157° which was identified as 2 : 3-dimethyl-2 : 3-di-*p*-tolylbutane (III). The by-product was probably formed by the dimerisation of two free radicals of dimethyl-*p*-tolylmethyl (II) the formation of which from *p*-cymene was initiated by the presence of ascaridole.



2 : 3-Dimethyl-2 : 3-di-*p*-tolylbutane was prepared by bubbling oxygen through specially purified *p*-cymene in the presence of a catalyst; [2] the use of commercial samples of *p*-cymene, even after fractional distillation, gave gummy residues instead of the desired product.

Experimental.—By-product in the formation of ascaridole glycol anhydride. A solution of ascaridole (30 g.) (purified by the method of Beckett *et al.*[3]) in *p*-cymene (60 g.) (purified by the method of Pines *et al.*[2]) was added dropwise to *p*-cymene (40 g.) boiling under reflux, and the mixture refluxed for 18 hr. Subsequent distillation gave *p*-cymene, b. p. 78—80°/25 mm., ascaridole glycol anhydride, b. p. 79—80°/0·5 mm., and a residue which recrystallised from ethanol as needles, m. p. 157° (0·49 g.), and was 2 : 3-dimethyl-2 : 3-di-*p*-tolylbutane [Found: C, 90·2, 90·5; H, 9·7, 9·7%; *M* (ebullioscopic in acetone), 257, 259. Calc. for $C_{20}H_{26}$: C, 90·2; H, 9·8%; *M*, 266].

The m. p. and the infrared and the ultraviolet absorption curve of the above crystalline product were identical with those of 2 : 3-dimethyl-2 : 3-di-*p*-tolylbutane prepared as reported below; a mixture of the latter with the crystalline product was undepressed in m. p.

p-Cymene (100 g.) alone, or with ascaridole (1 g.), when refluxed as above gave 35 and 54 mg. respectively of 2 : 3-dimethyl-2 : 3-di-*p*-tolylbutane. Refluxing *p*-cymene (100 g.) alone, and *p*-cymene (100 g.) with ascaridole glycol anhydride (10 g.), both in the dark, gave negligible residues of by-product.

2 : 3-*Dimethyl*-2 : 3-*di*-p-*tolylbutane.* As described by Pines *et al.*,[2] *p*-cymene (60 g.) was heated with coarse aluminium powder (50 g.) and anhydrous potassium carbonate (2 g.) under reflux for 18 hr. whilst oxygen was bubbled in at the rate of 12 l./hr., giving 2 : 3-dimethyl-2 : 3-di-*p*-tolylbutane (0·9 g.), m. p. 157°.

Oxidation. Oxidation [4] of the by-product (100 mg.), and of 2 : 3-dimethyl-2 : 3-di-*p*-tolylbutane (100 mg.), with nitric acid (3 ml. 25% w/w) at 190° for 18 hr. gave residues (75 mg.)

[1] Thoms and Dobke, *Arch. Pharm.*, 1930, **268**, 128.
[2] Pines, Kvetinskas, and Ipatieff, *J. Amer. Chem. Soc.*, 1955, **77**, 343.
[3] Beckett, Donbrow, and Jolliffe, *J. Pharm. Pharmacol.*, 1955, **7**, 55.
[4] Campbell, Soffer, and Steadman, *J. Amer. Chem. Soc.*, 1942, **64**, 426.

which, after being washed and dried, had m. p. >300° (with sublimation) and equiv. 84·0 and 83·7 respectively [Calc. for $C_6H_4(CO_2H)_2$: equiv., 83·0]. The dimethyl esters had m. p. 140° alone or mixed with dimethyl terephthalate.

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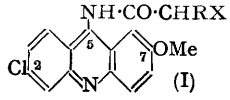
224. *2-Chloro-5-α-halogenoacylamino-7-methoxyacridines.*

By M. NEEMAN.

5-AMINO-2-CHLORO-7-METHOXYACRIDINE was acylated with α-halogenoacyl halides to yield the amides (I; R = H or Me, X = Cl or Br). The α-halogen atom in (I; R = H, X = Cl or Br) did not react with boiling diethylamine, in contrast to the analogous 6-methoxy-8-halogenoacetamidoquinolines.[1]



Experimental.—*2-Chloro-5-chloroacetamido-7-methoxyacridine* (I; R = H, X = Cl) was prepared by the addition of chloroacetyl chloride (1·1 g., 0·01 mol.) in chloroform (10 ml.) at −5° to a suspension of finely powdered 5-amino-2-chloro-7-methoxyacridine (2·6 g., 0·01 mol.) in chloroform (20 ml.) and pyridine (1 ml.). After 15 hr. at 30°, the product was filtered off, washed with dilute aqueous ammonia and water, and crystallised from 60% formic acid as yellow needles, m. p. 315° (decomp.) (Found: C, 56·9; H, 3·9; N, 8·6. $C_{16}H_{12}O_2N_2Cl_2$ requires C, 57·3; H, 3·6; N, 8·4%).

5-Bromoacetamido-2-chloro-7-methoxyacridine (I; R = H, X = Br) was prepared in an analogous manner by using bromoacetyl bromide, and crystallised from 60% formic acid in yellow needles, m. p. 330° (decomp.) (Found: C, 50·4; H, 3·6; N, 7·5. $C_{16}H_{12}O_2N_2BrCl$ requires C, 50·6; H, 3·2; N, 7·4%).

Both halogenoacetamido-compounds were recovered unchanged after 30 hours' refluxing with excess of diethylamine.

5-α-Bromopropionamido-2-chloro-7-methoxyacridine (I; R = Me, X = Br) was prepared in an analogous manner by using α-bromopropionyl bromide, and crystallised from acetone–ethanol as yellow needles, decomp. >360° (Found: C, 51·5; H, 4·0. $C_{17}H_{14}O_2N_2BrCl$ requires C, 51·8; H, 3·6%).

RESEARCH COUNCIL OF ISRAEL, JERUSALEM.

[*Received, September 13th,* 1955.]

[1] Neeman, *J.*, 1955, 2525.

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225. *Tracer Studies on Ester Hydrolysis. Part III.* The Alkaline Hydrolysis of Phenyl Benzoate.*

By C. A. BUNTON and D. N. SPATCHER.

IN some recent work [1] the alkaline hydrolysis of phenyl benzoate enriched in ^{18}O was used to locate the position of the tracer. It was assumed that one oxygen atom of the benzoic acid came from the water and the other from the ester, *e.g.*,

$$Ph{\cdot}C^{18}O{\cdot}OPh + OH^- \longrightarrow Ph{\cdot}C^{18}O{\cdot}O^- + Ph{\cdot}OH$$

This assumption has been tested by hydrolysing phenyl benzoate with sodium hydroxide, at 0°, in 50% aqueous dioxan, with the water isotopically enriched in ^{18}O. At intervals, unhydrolysed ester was isolated and its isotopic abundance measured. There

* Part II, *J.*, 1955, 1522.

[1] Bunton, Lewis, and Llewellyn, *J.*, in the press.
[2] Bender, *J. Amer. Chem. Soc.*, 1951, **73**, 1626.

was no appreciable oxygen exchange with water, whereas for the hydrolysis of alkyl benzoates the exchange rate is *ca.* 20% of that of hydrolysis.[2]

$$R'\cdot CO_2R + {}^{18}OH^- \rightleftharpoons R'\cdot C(O^-)({}^{18}OH)\text{–}OR \longrightarrow R'\cdot CO_2^- + ROH$$

(I.)

Therefore the intermediate (I), if formed, either loses the phenoxide rather than the hydroxide ion, or its life is too short for the two oxygen atoms to become equivalent by proton transfer. The present experiments do not differentiate between these possibilities. To allow calculation of the extent of hydrolysis the kinetics were followed over a limited range of alkali concentration; this alkaline hydrolysis of phenyl benzoate is much faster than that of the alkyl benzoates. The acid reaction is very slow.

Experimental.—The hydrolyses were followed by acid–base titration in aqueous dioxan (50% by volume), at 0°. Preliminary experiments showed that the reaction in acid solution was much slower than with hydroxyl ion; with N/40-hydrochloric acid, *ca.* 5% of the ester decomposed in 20 hr. at 25°. The reaction was therefore stopped by addition of *ca.* 0·1N-hydrochloric acid which was back-titrated, methyl-red–bromocresol-green being used. The rate coefficients were calculated graphically from the equation $k_2t(b - 2a) = \log_e a(b - 2x)/b(a - x)$, where a and b were the initial molar concentrations of ester and hydroxyl ion, respectively, and $(a - x)$ was the molar concentration of ester at time t. An example of a kinetic run is given below.

Temp. 0°; [Ester] = 0·0294M; [OH^-] = 0·0874M

Time (min.)	3·5	5	7	10	14	20	30
Reaction (%)	24·1	28·9	34·8	42·5	49·5	58·1	68·0
$\log_{10}\frac{b-2x}{a-x}$ found	0·5152	0·5275	0·5424	0·5664	0·5930	0·6355	0·7028
$\log_{10}\frac{b-2x}{a-x}$ reqd.	0·5150	0·5270	0·5410	0·5630	0·5920	0·6360	0·7060

$10^3k_2 = 9·9$ mole^{-1} l. sec.$^{-1}$.

The second-order rate coefficients (which were dependent on [OH^-]) were :

Run	[Ester], M	[OH^-], M	10^3k_2 (mole^{-1} l. sec.$^{-1}$)
1	0·0262	0·0435	13·0
2	0·0294	0·0874	9·9
3	0·0295	0·0965	9·7

Isolation of unchanged ester. Hydrolysis was carried out under kinetic conditions, with water enriched in ^{18}O. At intervals, reaction was stopped by addition of excess of hydrochloric acid, and the precipitated ester washed and recrystallised from aqueous alcohol. The purified esters were pyrolysed, over carbon *in vacuo*, to carbon monoxide, and this gas analysed mass-spectrometrically. A run, carried out under the conditions of kinetic run 1 and with the isotopic abundance of the water 0·383 atom-% excess, gave ester, isolated at various values of %-reaction, with the following excess of isotopic abundances, 15% reaction, 0·003%; 35% reaction, 0·005%; 55% reaction, 0·005%; 75% reaction, 0·006%. A second run with [Ester] = 0·04M, [OH^-] = 0·129M, and isotopic abundance of water = 2·80 atom-% excess, gave ester (m. p. 69°), isolated at 75% reaction, of 0·002 atom-% excess. In a confirmatory experiment a sample of benzoic acid (m. p. 121°) was isolated from an alkaline hydrolysis, with enriched water (isotopic abundance, 0·525 atom-% excess) its abundance was 0·260 atom-% excess.

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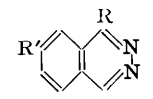
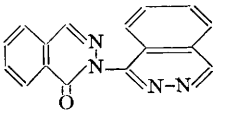
226. *Some Reactions in the Phthalazine Series.*

By C. M. Atkinson, C. W. Brown, and (the late) J. C. E. Simpson.

The preparation of 1-aminophthalazine (I; R′ = H, R = NH_2) has not been described although some physical constants are recorded.[1] Systematic investigation of the reaction conditions was needed before 1-chlorophthalazine (I; R′ = H, R = Cl) was prepared in consistently good yields from the hydroxy-compound. 1-Phenoxyphthalazine (I; R′ = H, R = OPh), prepared from the chloro-compound, was converted into the amine. As expected, 1-chlorophthalazine was stable to alkali at room temperature but with 5N-hydrochloric acid gave the hydroxy-compound, whereas more dilute acid yielded a compound which has been represented[2] by the structure (II) since the completion of this work.

(I)   (II)

1-Acetamidophthalazine was obtained from the amine by use of pyridine–acetic anhydride (but not of acetic anhydride alone) and readily formed a methiodide which on acid hydrolysis gave 1-aminophthalazine methiodide, identical with that prepared directly from the base.

1-Amino-7-nitrophthalazine (I; R′ = NO_2, R = NH_2) was prepared by a similar route to that leading to the *Bz*-unsubstituted compound. The nitrophthalaldehydic acid was prepared by the known method[3] but with modified bromination of 6-nitrophthalide. 1-Hydroxy-7-nitrophthalazine (I; R′ = NO_2, R = OH) was converted by phosphoryl chloride into the 1-chloro-derivative which resinified on attempted recrystallisation. As in the case of the *Bz*-nitro-4-phenoxycinnolines,[4] 7-nitro-1-phenoxyphthalazine (I; R′ = NO_2, R = OPh) was best prepared by using ammonium carbonate (rather than potassium hydroxide) in phenol. The phenoxy-compound, on treatment with molten ammonium acetate, gave 1-amino-7-nitrophthalazine which behaved as did the *Bz*-unsubstituted compound toward acetylating reagents and provided a dark red methiodide.

Experimental.—1-*Chlorophthalazine.* The hydroxy-compound (5 g.; m. p. 181—182°) was heated with phosphoryl chloride (15 c.c.) until boiling began. Refluxing was continued for *ca.* 2 min. Solid began to separate. The mixture was shaken until precipitation was complete (4 min.), then was poured into stirred 2N-sodium hydroxide (500 c.c.) and crushed ice (500 c.c.). The chloro-compound (4·2—4·7 g.), m. p. 109—111°, was washed with water and dried *in vacuo* over sodium hydroxide. In 7 of 8 experiments the yield was >70% (average 78%). Shorter heating reduced the yield. Gabriel and Neumann's[5] conditions never gave a yield of more than 46% (they claim 75%).

1-*Phenoxyphthalazine.* Finely powdered 1-chlorophthalazine (4·4 g.) was heated with potassium hydroxide (1·8 g., 1·2 mols.) in phenol (30 g., 7·5 mols.) on the steam-bath for 1 hr., cooled, and poured into 40% sodium hydroxide solution. The clear solution was diluted to *ca.* 300 c.c. and the yellow granular product (5·4 g., 91%) was collected. Pure 1-*phenoxyphthalazine*, m. p. 107—108°, was obtained by recrystallisation from ethanol (Found: C, 75·6; H, 4·75; N, 12·8. $C_{14}H_{10}ON_2$ requires C, 75·7; H, 4·5; N, 12·6%).

1-*Aminophthalazine.* Crude 1-phenoxyphthalazine (4 g.) was heated with molten ammonium acetate at 150—160° for 30 min. The amino-compound (2·5 g., 92%), m. p. 212—213°, was isolated by trituration of the cold mixture with water, in which the amine is appreciably soluble. Recrystallisation from nitromethane gave pure 1-*aminophthalazine*, m. p. 212—213°, as colourless needles (Found: C, 66·1; H, 5·0; N, 29·0. $C_8H_7N_3$ requires C, 66·2; H, 4·9; N, 28·9%).

[1] Albert, Goldacre, and Phillips, *J.*, 1948, 2240.
[2] Badger, McCarthy, and Rodda, *Chem. and Ind.*, 1954, 964.
[3] Borsche, Diacont, and Hanau, *Ber.*, 1934, **67**, 675.
[4] Keneford and Simpson, *J.*, 1948, 354.
[5] Gabriel and Neumann, *Ber.*, 1893, **26**, 521.

To a suspension of the amine (1 g.) in pyridine (8 c.c.) was added acetic anhydride (3 c.c.), and the mixture set aside for 3 hr., then evaporated to dryness in a desiccator, and the product isolated by treatment with acetone. 1-*Acetamidophthalazine*, m. p. 183—184°, separated from ethanol in colourless needles (Found : C, 64·1; H, 4·7; N, 22·9. $C_{10}H_9ON_3$ requires C, 64·15; H, 4·8; N, 22·45%). Heating this (0·21 g.) with ethanol (4 c.c.) and methyl iodide (2 c.c.) gave the *methiodide* which separated from water as pale yellow rods, m. p. 253—254° (depressed to 220° on admixture with the 1-amino-salt, m. p. 251—252°) (Found : C, 40·45; H, 3·75; N, 13·0; I, 43·95. $C_{11}H_{12}ON_3I$ requires C, 40·15; H, 3·7; N, 12·8; I, 38·6%).

1-*Aminophthalazine methiodide*. (*a*) The amino-compound (1 g.), methanol (5 c.c.), and methyl iodide (2 c.c.) were refluxed for 4 hr. and the solution was set aside for crystallisation (30 min.; 0·73 g.). Recrystallisation from water gave the *methiodide*, m. p. 251—252° (0·68 g.), as pale yellow needles (Found : C, 37·7; H, 3·65; N, 14·5; I, 43·05. $C_9H_{10}N_3I$ requires C, 37·6; H, 3·5; N, 14·6; I, 44·2%). The mother liquor yielded unchanged base (0·49 g.), m. p. 200—205°.

(*b*) 1-Acetamidophthalazine methiodide (0·15 g.) was refluxed with N-hydrochloric acid (1 c.c.) for 1 hr., the solution was cooled, and the methiodide (0·1 g.), m. p. and mixed m. p. 251—252°, collected.

2-*Formyl*-5-*nitrobenzoic acid*. 6-Nitrophthalide (14·4 g.)[3] was kept at 175—180° and bromine (10·6 c.c.) passed in during 2 hr. in a stream of carbon dioxide. The dark red resinous product was boiled with water (*ca.* 200 c.c.) for 45 min. (a small amount of insoluble tar remained) and treated with carbon. The aldehydo-acid separated as pale yellow needles (10·1 g.), m. p. 156—160°. The acid yielded a 2 : 4-dinitrophenylhydrazone, m. p. 288—290° (decomp.) (lit., m. p. 290°). The recorded method of bromination [3] gave only unchanged material.

1-*Hydroxy*-7-*nitrophthalazine*. A solution of the above acid (10·1 g.) in 95% ethanol (300 c.c.) was heated with 36·5% aqueous hydrazine (4·6 c.c.) for 1 hr. The *phthalazine* (7·6 g.), m. p. 232—233°, separated on cooling (Found : C, 50·45; H, 2·55; N, 22·05. $C_8H_5O_3N_3$ requires C, 50·3; H, 2·6; N, 22·0%). This compound is insoluble (sodium salt) in 2N-sodium hydroxide but soluble in more dilute (*ca.* N/30) alkali; it crystallises from ethanol or nitromethane as pale yellow needles.

1-*Chloro*-7 *nitrophthalazine*. The hydroxy-compound (3 g.) was heated on the steam-bath for 1 hr. with phosphoryl chloride (9 c.c.), and the mixture poured into stirred aqueous sodium hydroxide (300 c.c.) and crushed ice (300 c.c.). The pale yellow solid was extracted with chloroform and the extract washed with 2N-sodium hydroxide and water, dried, and evaporated to give the crude chloro-compound (2·55 g.), m. p. 155—157° (decomp.).

7-*Nitro*-1-*phenoxyphthalazine*. The foregoing chloro-compound (4·8 g.), ammonium carbonate (6·5 g.), and phenol (14·4 g.) were heated on the steam bath for 45 min. and poured into 2N-sodium hydroxide. The brown solid formed from the initial oil was filtered off and yielded material, m. p. 204—207° (5·05 g.), by successive digestion with small portions of water and ethanol. The *phenoxy-compound*, m. p. 212—213°, separated from chloroform–light petroleum (b. p. 60—80°) as pale yellow needles (Found : C, 62·75; H, 3·4; N, 15·65. $C_{14}H_9O_3N_3$ requires C, 62·9; H, 3·4; N, 15·7%).

1-*Amino*-7-*nitrophthalazine*. This was prepared from the phenoxy-derivative (2·4 g.) as for the *Bz*-unsubstituted compound (185—190° for 15 min.). The melt was cooled, diluted with water, and basified with concentrated aqueous ammonia, and the solid was purified by dissolution in 30—40% acetic acid (charcoal) and precipitation by ammonia. The resulting bright yellow granular *amine* (1·4 g.) crystallised from aqueous methanol as needles, m. p. 303—304° (decomp.) (Found : C, 48·4; H, 3·95; N, 27·75. $C_8H_6O_2N_4,\frac{1}{2}H_2O$ requires C, 48·2; H, 3·5; N, 28·1%). This gave, as above, the *acetyl derivative*, yellow needles, m. p. 252—253° (from methanol) (Found : C, 52·05; H, 3·5; N, 24·2. $C_{10}H_9O_3N_4$ requires C, 51·65; H, 3·5; N, 24·1%).

1-*Amino*-7-*nitrophthalazine methiodide*, prepared in the usual manner and recrystallised (3 times) from water, had m. p. 251—252° (Found : C, 32·75; H, 2·75; N, 16·8; I, 38·45. $C_9H_9O_2N_4I$ requires C, 32·6; H, 2·7; N, 16·9; I, 38·2%).

2-*Methyl*-7-*nitro*-1-*phthalazone*. A solution of 1-hydroxy-7-nitrophthalazine (0·2 g.) in 0·5N-sodium hydroxide (3 c.c.) and water (40 c.c.) was shaken with methyl sulphate (0·1 c.c.) and set aside for 15 min. after pale yellow needles (0·11 g.) began to separate. The pure *phthalazone*, m. p. 177—179°, crystallised from ethanol (Found : C, 53·1; H, 2·95; N, 20·5. $C_9H_7O_3N_3$ requires C, 52·7; H, 3·4; N, 20·5%).

1-*Methoxy*-7-*nitrophthalazine*. Crude 1-chloro-7-nitrophthalazine (0·15 g.), methanol (3 c.c.) and methanolic sodium methoxide (3 c.c. containing 0·045 g. of methoxide) were refluxed for 30 min., then poured into water. Extraction with ether and evaporation of the washed, dried,

and clarified (charcoal) extract left a sticky solid (0·12 g.). Repeated recrystallisation from aqueous ethanol gave the *methoxy-derivative*, m. p. 175—176°, as light brown needles (Found : C, 52·9; H, 3·95; N, 20·6. $C_9H_7O_3N_3$ requires C, 52·7; H, 3·4; N, 20·5%). A mixed m. p. with the isomeric phthalazone (above) was 130—135°.

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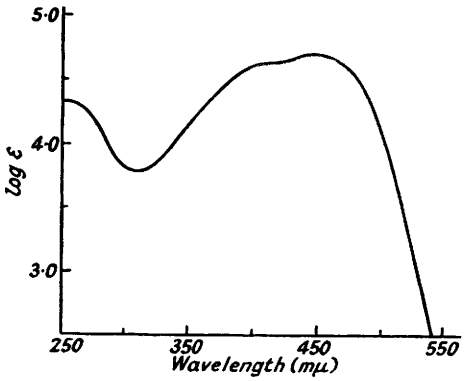
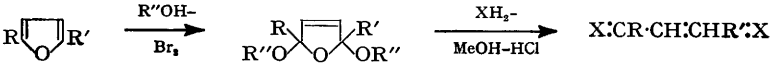
227. *Ultraviolet Absorption Spectra of 2 : 4-Dinitrophenylhydrazones of Conjugated Alkenediones.*

By K. G. LEWIS.

DURING work involving a reaction with 2 : 4-dinitrophenylhydrazine, a substance was isolated for which one possible formulation was the bis-2 : 4-dinitrophenylhydrazone of a compound of type R·CO·CH:CH·CO·R′ (I). Although the ultraviolet absorption spectra of the 2 : 4-dinitrophenylhydrazones of conjugated unsaturated monocarbonyl compounds



are well established,[1,2] there appeared to be no record of ultraviolet absorption spectra of 2 : 4-dinitrophenylhydrazones derived from the type of compound (I). Compounds having the required absorbing system were readily prepared by the following route :



(II) (III)

[X = $(NO_2)_2C_6H_3$·NH·N=.]

The absorption curve for the compound (III ; R = H, R′ = CH_2·OMe) in dioxan is shown in the Figure ; curves for three other substances were very similar. They show no well-defined peak, only a broad intense band in the region 400—460 mμ (log ε 4·6—4·7) and this seems characteristic of this conjugated chromophore.

Experimental.—*2 : 5-Dialkoxy-2 : 5-dihydrofurans.* Except the parent (II ; R = R′ = H) these were prepared by the action of bromine and methanol on the corresponding furan according to the directions of Clauson-Kaas.[3] The parent (II ; R = R′ = H) was prepared

[1] Braude and Jones, *J.*, 1945, 498.
[2] Gillam and Stern, "An Introduction to Electronic Absorption Spectroscopy," Arnold, London, 1954.
[3] Clauson-Kaas, *Kgl. danske Videnskab. Selskab, Mat.-fys. Medd.*, 1947, **24**, 6.

by Mr. V. R. Stimson by the action of *tert.*-butyl hypochlorite in *tert.*-butanol on furan, which gave no isolable product with bromine and *tert.*-butanol. 2 : 5-Dihydro-2 : 5-dimethoxy-2-methylfuran had b. p. 61—62°/20 mm., n_D^{22} 1·4296 (lit.,[4] b. p. 46°/8 mm., n_D^{25} 1·4265) (Found : C, 58·6; H, 8·8; OMe, 41·3. Calc. for $C_7H_{12}O_3$: C, 58·3; H, 8·4; OMe, 43·0%). 2 : 5-Dihydro-2 : 5-dimethoxy-2-methoxymethylfuran had b. p. 92°/15 mm., n_D^{17} 1·4430 (lit.,[5] 84—85°/10 mm., n_D^{25} 1·4383) (Found : C, 55·3; H, 8·1. Calc. for $C_8H_{14}O_4$: C, 55·2; H, 8·1%).

Bis-2 : 4-*dinitrophenylhydrazones of alkenediones.* The dialkoxydihydrofuran (0·5 ml.) was added dropwise to 2 : 4-dinitrophenylhydrazine (1 g.) in boiling methanol (100 ml.) containing concentrated hydrochloric acid (1 ml.). The red powder that slowly separated was washed with methanol and recrystallised, yielding red *bis*-2 : 4-*dinitrophenylhydrazones* of malealdehyde, needles (from nitromethane), m. p. 300° (decomp.) (Found: C, 43·2; H, 2·9. $C_{16}H_{12}O_8N_8$ requires C, 43·25; H, 2·7%), 4-oxopent-2-enal, needles (from nitrobenzene–tetrachloroethane), m. p. 269° (decomp.) (Jones[6] records m. p. 270°) (Found : C, 45·1; H, 3·2; O, 27·6; N, 24·1. Calc. for $C_{17}H_{14}O_8N_8$: C, 44·5; H, 3·1; O, 27·95; N, 24·45%); 5-methoxy-4-oxopent-2-enal (from nitrobenzene–tetrachloroethane), m. p. 259° (decomp.) (Found : C, 44·1; H, 3·5; OMe, 6·0. $C_{18}H_{16}O_9N_8$ requires C, 44·3; H, 3·3; OMe, 6·35%), and hex-3-ene-2 : 5-dione, needles (from nitromethane), m. p. 289—289·5° (decomp.) (Jones[6] records m. p. 290°) (Found : C, 46·0; H, 3·4. Calc. for $C_{18}H_{16}O_8N_8$: C, 45·8; H, 3·4%).

Absorption spectra were measured on a Hilger Uvispek. Dioxan was purified as recommended by Fieser.[7]

The microanalyses were carried out by Dr. K. W. Zimmermann of the C.S.I.R.O. Microanalytical Laboratory, Melbourne.

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[4] Clauson-Kaas, Limborg, and Dietrich, *Acta Chem. Scand.*, 1952, **6**, 545.
[5] Clauson-Kaas, *ibid.*, p. 556.
[6] Jones, B.P., 595,041/1945.
[7] Fieser, " Experiments in Organic Chemistry," Heath and Co., New York, 2nd Edn., p. 369.

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228. *A Direct-current Integrating Potentiometric Circuit for the Measurement of Small E.M.F.s developed across High Resistances.*

By J. I. CARASSO and R. W. PITTMAN.

MEASUREMENTS of E.M.F.s generated across high resistances are usually made with instruments involving electrometer triodes, as in commercial pH meters. An alternative method is described here which has been found advantageous for measurements on sources with resistances up to 10^{10} ohms such as specimens of grey selenium and some special glass electrodes.

The E.M.F. to be measured, E, is backed by the output of a D.C. potentiometer (Tinsley G.P. Type 3387B.) and the out-of-balance voltage is used to charge a condenser (T.C.C. " Plastapack," Type C.P.L.) for a time depending on the time-constant of the resistance–capacity circuit consisting of the source, R, and condenser, C (Fig. 1). The deflection obtained on discharging the condenser through a ballistic galvanometer, G, is plotted against the backing voltage, and the required E.M.F. is given by the intercept of the plot on the voltage axis.

The circuit must be efficiently guarded against stray charging currents which cause misleading results; adequate protection to obtain results for source resistances up to 10^9 ohms can be achieved by standing the apparatus on an earthed metal plate and using earthed-screen leads. If due allowance is made for the residual stray charging current (always $<10^{-12}$ A), E from sources of 10^{10} ohms can be measured to the nearest mv.

An estimate of the resistance of the source may be obtained from a ballistic measurement of the time-constant of the resistance–capacity circuit.

The quality of the results justifies the greater expenditure of time and the need to use a sensitive ballistic galvanometer. As shown in Fig. 2, it is possible to measure a potential difference across a source of resistance 10^{10} ohms to the nearest 1 mv, *i.e.*, to detect a power

of 10^{-16} w, a 4500 mm./μC galvanometer and a 0·1 μF condenser being used with allowance of a charging time of *ca.* 1 min.

If the resistance of the source does not exceed 10^8 ohms, measurements to the nearest 0·05 mV can readily be obtained with a 2 μF condenser. When an electronic pH meter, fitted with an external reflecting galvanometer, was used as a voltmeter across sources with

FIG. 1.

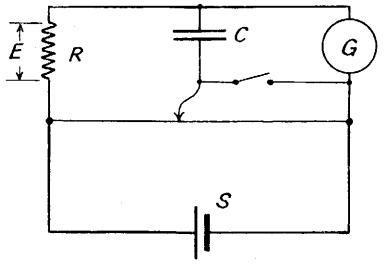
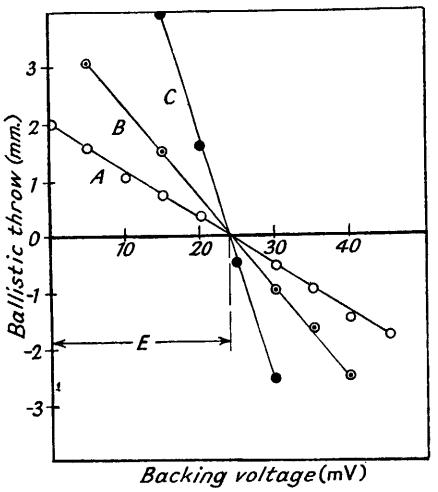


FIG. 2.



Charging time : *A*, 30 sec.; *B*, 1 min.; *C*, 2 min. $R = 10^{10}$ ohms. $C = 0{\cdot}1$ μF.

resistances as low as 5×10^7 ohms, readings could not be taken with an accuracy better than ±0·5 mV owing to external interferences.

Part of the success of the method appears to reside in the time integration of the total input signal, which cancels much of the random " noise " inherent in such measurements. The successful use of this simple principle is probably largely due to the excellent insulation resistance (over 10^6 ohm farad) and negligible residual charges and anomalous charging currents of the polystyrene film capacitors used.

One of us (J. I. C.) is indebted to the Engineer-in-Chief of the General Post Office for permission to use this information.

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