NOTES.

The Action of Benzaldehyde on Benzyloxyacetone: a New cyclo*Pentane Synthesis.*

By J. QUARTERMAN and T. S. STEVENS.

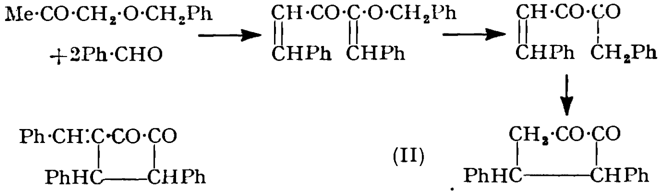
[Reprint Order No. 5844.]

CONDENSATION between the compounds mentioned in the title was investigated as a possible route to benzyloxymethyl styryl ketone, (I). In presence of either sodium hydroxide or hydrogen chloride, the rather sluggish reaction afforded a moderate yield of a ketonic, unsaturated liquid which approximated roughly in composition to the ketone (I) and gave no iodoform reaction. The acid-catalysed process gave in addition a solid, $C_{17}H_{14}O_2$, which was identified as the 1 : 2-diphenyl*cyclo*pentane-3 : 4-dione (II) described by von Liebig (*Annalen*, 1914, **405**, 188). The process may be formulated as shown.

The dibenzylidene derivative, as an enol ether, is hydrolysed to the unsaturated diketone, which then gives (II) by an internal Michael reaction. When more energetic acid conditions were used, the final product was the benzylidene derivative (III) of the diketone (II).

$CH_2Ph{\cdot}O{\cdot}CH_2{\cdot}CO{\cdot}CH{:}CHPh$

(I)



(III)

(II)

Benzyloxyacetone was not produced in tolerable yield by the Williamson synthesis or its variations, but good results were obtained by the route : $CH_2PhCl + CH_2O + KCN \longrightarrow CH_2Ph{\cdot}O{\cdot}CH_2{\cdot}CN \longrightarrow CH_2Ph{\cdot}O{\cdot}CH_2{\cdot}COMe$.

Experimental.—*Benzyloxyacetonitrile.* Powdered sodium cyanide (50 g.) was dissolved, with cooling, in a mixture of 40% aqueous formaldehyde (100 c.c.) and methanol (100 c.c.). After addition of benzyl chloride (110 c.c.) in methanol (200 c.c.) the mixture was heated until a gentle reaction set in, and refluxed for 5 min. thereafter. Water (250 c.c.) was added and the nitrile repeatedly extracted with ether–ligroin (b. p. 40—60°) (1 : 1). On distillation the extract gave crude nitrile, b. p. 130—170°/20 mm.; pure *benzyloxyacetonitrile* boiled at 140°/20 mm. (Found: C, 73·9; H, 6·1; N, 9·5. C_9H_9ON requires C, 73·5; H, 6·1; N, 9·5%). After concentration, the aqueous-alcoholic solution from which the nitrile had been extracted deposited a few g. of benzyloxyacetamide, long needles, m. p. 89—91° after recrystallisation from benzene–ligroin and from water (Found: N, 8·3. Calc. for $C_9H_{11}O_2N$: N, 8·5%). Darmon (*Compt. rend.*, 1933, **197**, 1328) gives m. p. 91°.

Benzyloxyacetone. Benzyloxyacetonitrile (15 g.) was added to ethereal methylmagnesium iodide from methyl iodide (29 g.) and magnesium (5 g.). After 16 hr. the mixture was treated with dilute sulphuric acid, and the ether extract was distilled. The fraction (10 g.), b. p. 118—134° (mostly at 130°), gave the iodoform test and still contained 0·2% of nitrogen. It afforded a 2 : 4-*dinitrophenylhydrazone*, orange-yellow needles, m. p. 92—93° (Found: N, 16·2. $C_{16}H_{16}O_5N_4$ requires N, 16·2%), and a *semicarbazone*, plates, m. p. 113—114° (Found: C, 60·0; H, 6·5; N, 19·4. $C_{11}H_{15}O_2N_3$ requires C, 59·7; H, 6·5; N, 19·0%); the slightly impure ketone was used in subsequent experiments. No benzyloxyacetone could be obtained from chloroacetone and sodium benzyl oxide. When chloroacetone (1 g.) and benzyl alcohol (1 g.) were heated for 3 hr. at 100° in presence of (*a*) pyridine (1 g.), (*b*) calcium carbonate (1 g.), (*c*) barium hydroxide (1 g.), or (*d*) calcium hydroxide (1 g.), the yield of benzyloxyacetone was respectively 21, 3, 35, and 14%, as determined in the fraction, b. p. 120—130°/20 mm., of neutral material by Vandoni and Desseigne's hydroxylamine method (*Bull. Soc. chim. France*, 1935, **11**, 1685). These materials gave the dinitrophenylhydrazone described above.

Condensation with benzaldehyde. (*a*) Benzyloxyacetone (15 c.c.) and benzaldehyde (7 c.c.) were heated with 25% aqueous sodium hydroxide (2 c.c.) and enough dioxan to form a homogeneous solution, for 72 hr. at 100°. The product, dissolved in ether, washed, and distilled, gave a yellow oil (5 g.), b. p. 205—215°/14 mm. (mostly 210—212°). (*b*) Dry hydrogen chloride was passed for 5 min. into a mixture of benzyloxyacetone (6 g.) and benzaldehyde (2·3 g.). After 24 hr. the mixture was dissolved in ether, washed with sodium hydrogen carbonate solution, and distilled. The resulting yellow oil, b. p. 210—220°/20 mm., deposited yellow crystals which were washed with ligroin. The remaining oil, repeatedly distilled, boiled at 205—208°/12 mm. [Found: C, 78·5; H, 6·6%; *M* (Rast), 225. Calc. for $C_{17}H_{16}O_2$: C, 80·9; H, 6·3%; *M*, 252]. The yellow solid crystallised from ethanol (charcoal) in colourless needles, saturated to bromine and permanganate (Found: C, 81·5; H, 5·6. Calc. for $C_{17}H_{14}O_2$: C, 81·6; H, 5·6%). The m. p., 176—177°, was not depressed on admixture with diphenyl*cyclo*pentanedione prepared by von Liebig's method; the two preparations also afforded identical diacetyl derivatives, m. p. and mixed m. p. 145°. (*c*) A stream of dry hydrogen chloride was passed for 3 hr. through a mixture of benzyloxyacetone (14 g.) and benzaldehyde (8 g.), and the whole kept at room temp. for 48 hr. When shaken with ether and sodium hydrogen carbonate solution it deposited a yellow powder (9 g.) which crystallised from acetic acid in needles, m. p. 219—221°, very sparingly soluble in ethanol (Found: C, 84·5; H, 5·4. Calc. for $C_{24}H_{18}O_2$: C, 85·2; H, 5·3%). von Liebig reports that benzylidenediphenyl*cyclo*pentanedione melts at 223° and is difficult to burn quantitatively.

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THE UNIVERSITY, SHEFFIELD. [*Received, November 3rd*, 1954.]

The Preparation of p-*Di-(6-carboxyhexanoyl)benzene.*

By G. D. PARKES and K. J. CLARK.

[Reprint Order No. 6082.]

THE sodium derivative of tri(tetrahydro-2-pyranyl) pentane-1 : 1 : 5-tricarboxylate reacts with terephthaloyl dichloride in benzene. Decomposition of the product with acetic acid gives a small yield of *p*-di-(6-carboxyhexanoyl)benzene. Attempts to prepare *p*-di-(4-carboxybutanoyl)benzene by a similar method, using propane-1 : 1 : 3-tricarboxylic acid, were unsuccessful. The use of the benzyl ester method was unsuccessful for both acids (cf. Bowman, *J.*, 1950, 325; Bowman and Fordham, *Chem. and Ind.*, 1951, 742; *J.*, 1952, 3945). These experiments are the preliminary to an attempt to synthesise interlocking carbon rings.

Experimental.—Ethyl δ-bromovalerate was prepared from ethyl hydrogen adipate by the procedure recorded for the methyl ester (*Org. Synth.*, 1946, **26**, 52; Archer and Pratt, *J. Amer. Chem. Soc.*, 1944, **66**, 1656; Hunsdiecker, *Ber.*, 1942, **75**, 291; Merchant *et al.*, *J. Amer. Chem. Soc.*, 1927, **49**, 1828). The yield of ester, b. p. 120°/15 mm., 129°/35 mm., was 51%.

Triethyl pentane-1 : 1 : 5-tricarboxylate was prepared by the interaction of δ-bromovaleric ester and sodiomalonic ester according to the method of Cheney and Piening (*J. Amer. Chem. Soc.*, 1945, **67**, 931) who used δ-chlorovaleric ester. The yield of ester, b. p. 177—184°/13—15 mm., was 69%. Pentane-1 : 1 : 5-tricarboxylic acid was then obtained by their method (*loc. cit.*).

p-*Di-(6-carboxyhexanoyl)benzene* (cf. Bowman and Fordham, *loc. cit.*). Pentane-1 : 1 : 5-tricarboxylic acid (10·2 g., 0·05 mole) was added in small portions to a solution of redistilled dihydropyran (18 g., 0·225 mole) in " AnalaR," sodium-dried benzene (50 ml.) containing 1 drop of concentrated sulphuric acid at <30°, with exclusion of moisture. After one day, the resulting clear solution was freed from traces of free acid by shaking it with solid potassium hydroxide (4 g.) for 0·5 hr., the solution was decanted, and the solvent and excess of dihydropyran were removed by distillation under reduced pressure at <30°.

The residual ester in benzene (50 ml.) was added to sodium powder (1·15 g.) in benzene (100 ml.) at <35°. When the sodium had dissolved, terephthaloyl chloride (4·9 g., 0·02 mole) in benzene (50 ml.) was added. After storage with occasional shaking for 1 hr. and stirring for a further 1½ hr., acetic acid (6 ml.) was added and the mixture boiled until evolution of carbon dioxide ceased. The cooled mixture was washed with water. A white solid, insoluble in both layers, was precipitated : when recrystallised from water this had m. p. 185—195°. The aqueous layer, saturated with salt and extracted with ether, yielded nothing. The benzene layer, when dried overnight over sodium sulphate, deposited thereon a solid, which was separated by dissolving the whole solid in boiling water and cooling : this product had m. p. 185—195°. The benzene was removed under pressure, an oil (b. p. 90—95°/30 mm., 6·85 g.) distilling; the residual yellow solid did not crystallise from alcohol or acetic acid but separated therefrom as an amorphous powder, m. p. 205—230°; analysis indicated that it was a mixture of mono- and di-acids (Found : C, 64·9; H, 6·8. Calc. for $C_{14}H_{16}O_5$: C, 63·6; H, 6·1. Calc. for $C_{20}H_{26}O_6$: C, 66·3; H, 7·2%). Separation was achieved by fractional extraction with boiling water (21 × 200 ml.). Material separating from the last eleven fractions was combined and appeared to consist of p-*di-(6-carboxyhexanoyl)benzene* (Found : C, 65·87; H, 7·1. $C_{20}H_{26}O_6$ requires C, 66·3; H, 7·2%), though no determination of equivalent weight was made.

Propane-1 : 1 : 3-tricarboxylic ester was obtained according to the directions of Ruzicka *et al.* (*Helv. Chim. Acta*, 1934, **17**, 183) and converted into the acid by Cheney's method (*loc. cit.*).

The authors thank Sir Robert Robinson for his interest and advice.

DYSON PERRINS LABORATORY, OXFORD. [*Received January 28th*, 1955.]

The Synthesis and Cleavage of 9-Phenanthryl Phenyl Ether.

R. L. HUANG.

[Reprint Order No. 6157.]

9-PHENANTHRYL PHENYL ETHER has been prepared by the method of Ullmann and Sponagel (*Ber.*, 1905, **38**, 2212) and subjected to treatment with reagents known to cleave diaryl ethers, namely, sodium in liquid ammonia, and Grignard reagents at elevated temperatures or in the presence of anhydrous cobaltous chloride (cf. Huang, *J.*, 1954, 3084).

Reaction with a large excess of sodium in liquid ammonia gave quantitative yields of phenol and 9 : 10-dihydrophenanthrene, although when only two atoms of the metal were used no phenolic material could be isolated. Since phenanthrene is known to undergo reduction under the same conditions (Hückel and Bretschneider, *Annalen*, 1939, **540**, 183), these results strongly suggest that in the case of the phenanthryl ether the reaction which first took place exclusively was reduction of the phenanthrene nucleus at the 9 : 10-position, the reduced ether then suffering cleavage to phenol with excess of sodium, as would a substituted benzyl ether.

Heating the ether with methylmagnesium iodide at 200° resulted in a complex mixture from which were obtained phenol (corresponding to a 4% cleavage), unchanged ether (51%), and intractable oils. Cleavage by *n*-butylmagnesium bromide and cobaltous chloride in the manner previously described (Huang, *loc. cit.*) occurred only to a small extent (10%), yielding a mixture of phenol and 9-phenanthrol in a molar ratio of 76 : 24. It is not certain whether reduction of the phenanthrene nucleus occurred before cleavage; if it had, it could not have been extensive, since an attempt to isolate 9 : 10-dihydrophenanthrene by chromatography was unsuccessful. (Phenanthrene itself was found to be unaffected by this treatment.) The relatively high proportion of phenol seems to be a common feature with two other polynuclear aryl ethers so far studied, namely, α- and β-naphthyl phenyl ether, the former giving on cleavage 69 mole % of phenol (Kharasch and Huang, *J. Org. Chem.*, 1952, **17**, 669) and the latter, 65 mole % (Huang, unpublished result).

Experimental.—*9-Phenanthryl phenyl ether.* 9-Bromophenanthrene (35 g.) was heated with a mixture of potassium hydroxide (10 g.) and phenol (31 g.) for 2 hr. at 250° (reaction being incomplete at 200° after 4 hr.). The *ether* was isolated by extraction with benzene and distilled (b. p. 201—210/1 mm.). It crystallised from benzene–ethanol in prisms, m. p. 80—81° (17 g.), and exhibited a violet fluorescence in solution (Found: C, 89·2; H, 5·3. $C_{20}H_{14}O$ requires C, 88·9; H, 5·2%).

Cleavage experiments. (*a*) 9-Phenanthryl phenyl ether (10·8 g.) in diethyl ether (75 c.c.) was added to a solution of methylmagnesium iodide (from 43 g. of methyl iodide and 7·7 g. of magnesium) in ether (150 c.c.). The solvent was distilled off and the mixture heated at 200° for 7 hr. After cooling, moist ether was added, followed by water and dilute sulphuric acid. The product was taken into ether and the phenolic fraction extracted with aqueous potassium hydroxide (10%, followed by 20%). This extract on acidification gave phenol (0·15 g.) which was steam-distilled, titrated iodometrically, and identified in the usual way. The neutral fraction was chromatographed on alumina, giving the starting material (5·5 g.) and small fractions of brown oils.

(*b*) 9-Phenanthryl phenyl ether (8·1 g.) was treated with *n*-butylmagnesium bromide (from 21 g. of *n*-butyl bromide and 3·6 g. of magnesium) and anhydrous cobaltous chloride (11 g.) in the usual way. From the product an alkali-soluble fraction was obtained which on steam-distillation gave, in the distillate, phenol (0·21 g.) and, in the residue, 9-phenanthrol (0·14 g.), m. p. 155—156° after recrystallisation from benzene–*cyclo*hexane (lit., m. p. 158°). The neutral fraction, on treatment with ethanol, deposited the unchanged phenanthryl ether (4·1 g.) which was filtered off. The filtrate was concentrated and adsorbed on alumina. Elution with benzene followed by benzene–acetone (20 : 1) gave more phenanthryl ether (*ca.* 1 g.) and small fractions of brown oils.

(*c*) 9-Phenanthryl phenyl ether (2·0 g.) in diethyl ether (*ca.* 20 c.c.) was added to liquid ammonia (*ca.* 200 c.c.). With vigorous stirring, sodium (2·5 g., 8 atoms per mole of ether) was added in small pieces during 1 hr., and after a further 2 hours' stirring powdered ammonium chloride was introduced. After evaporation of the ammonia followed by addition of water

(25 c.c.), the product was taken up in ether, and the phenolic fraction isolated by alkali-extraction and estimated in the usual manner, giving phenol (0·6 g.) but no phenanthrol. The neutral fraction was dissolved in light petroleum–benzene (1 : 1) and passed through a column of alumina, then distilled, giving 9 : 10-dihydrophenanthrene (1·3 g.) b. p. 92—97° (bath)/0·5 mm., n_D^{24} 1·6397 [Durland and Adkins report n_D^{25} 1·6406 (*J. Amer. Chem. Soc.*, 1937, **59**, 135)] (Found : C, 93·15, 93·0; H, 6·8, 6·8. Calc. for $C_{14}H_{12}$: C, 93·3; H, 6·7%). A similar reduction with only 2 atoms of sodium per mole of the ether gave no phenolic material.

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UNIVERSITY OF MALAYA, SINGAPORE. [*Received, February 19th*, 1955.]

Synthesis of β-Amino-sulphones and αβ-Unsaturated Sulphones.
*Part II.**

By M. BALASUBRAMANIAN, V. BALIAH, and T. RANGARAJAN.

[Reprint Order No. 6234.]

IN Part I *, the preparation of β-amino-sulphones and αβ-unsaturated sulphones by use of arylsulphonylacetic acids was described. The present communication deals with the preparation of similar compounds with alkylsulphonylacetic acids. The condensation of these acids with salicylaldehyde yielded 3-alkylsulphonylcoumarins (cf. Troger and Bolte, *J. prakt. Chem.*, 1921, **103**, 163; Tröger and Dunkel, *ibid.*, 1922, **104**, 311).

Experimental.—Alkylsulphonylacetic acids. The alkylthioacetic acids (Larsson, *Ber.*, 1930, **63**, 1347) were oxidised in acetone at room temperature by the addition of an excess of a 5%

TABLE 1. β-*Amino-sulphone hydrochlorides*, $R{\cdot}SO_2{\cdot}CH_2{\cdot}CHR'{\cdot}NH_2,HCl$.

No.	R′	Yield (%) *	M. p.	Formula	Found (%) C	Found (%) H	Found (%) Cl⁻	Required (%) C	Required (%) H	Required (%) Cl⁻
				R = Me						
1	Ph	(6) [a]								
2	3 : 4-$(CH_2O_2)C_6H_3$	11(10)	248—250° (d)	$C_{10}H_{13}O_4NS,HCl$	—	—	12·5	—	—	12·7
3	o-C_6H_4Cl	20(3)	195—197	$C_9H_{12}O_2NClS,HCl$	—	—	13·1	—	—	13·1
4	m-$NO_2{\cdot}C_6H_4$	14(16)	202—203	$C_9H_{12}O_4N_2S,HCl$	38·5	4·8	12·6	38·5	4·6	12·6
				R = Et						
5	Ph	(6) [a]								
6	3 : 4-$(CH_2O_2)C_6H_3$	20(5)	206—208 (d)	$C_{11}H_{15}O_4NS,HCl$	44·9	5·55	12·4	45·0	5·45	12·1
7	o-C_6H_4Cl	21 [b]	209—210	$C_{10}H_{14}O_2NClS,HCl$	—	—	12·1	—	—	12·5
8	o-$NO_2{\cdot}C_6H_4$	18(4)	220—222 (d)	$C_{10}H_{14}O_4N_2S,HCl$	41·2	5·0	11·9	40·9	5·1	12·1
9	m-$NO_2{\cdot}C_6H_4$	20(17)	146—148	$C_{10}H_{14}O_4N_2S,HCl$	—	—	12·1	—	—	12·1
10	o-$OH{\cdot}C_6H_4$	14 [c]	211—213 (d)	$C_{10}H_{15}O_3NS,HCl$	45·2	6·05	13·0	45·2	6·0	13·4
				R = Pr						
11	o-C_6H_4Cl	23(6)	208—210	$C_{11}H_{16}O_2NClS,HCl$	—	—	11·8	—	—	11·9
12	m-$NO_2{\cdot}C_6H_4$	30 [b]	144—146	$C_{11}H_{16}O_4N_2S,HCl,H_2O$	40·7	5·8	10·7	40·4	5·8	10·9
				R = Bu						
13	3 : 4-$(CH_2O_2)C_6H_3$	7 [b]	164—166	$C_{13}H_{19}O_4NS,HCl$	48·6	6·3	11·1	48·5	6·2	11·0
14	o-C_6H_4Cl	11 [b]	192—194	$C_{12}H_{18}O_2NClS,HCl,H_2O$	43·5	6·5	11·1	43·6	6·4	10·8
15	m-$NO_2{\cdot}C_6H_4$	12 [b]	182—184	$C_{12}H_{18}O_4N_2S,HCl$	44·5	5·9	10·8	44·65	5·9	11·0
				R = $PhCH_2$						
16	Ph	18(18)	223—224	$C_{15}H_{17}O_2NS,HCl$	—	—	11·6	—	—	11·4
17	3 : 4-$(CH_2O_2)C_6H_3$	(7) [a]	—	—	—	—	—	—	—	—
18	o-C_6H_4Cl	21(10)	226—228	$C_{15}H_{16}O_2NClS,HCl$	—	—	10·3	—	—	10·3
19	p-C_6H_4Cl	20(14)	228—230	$C_{15}H_{16}O_2NClS,HCl$	—	—	10·4	—	—	10·3
20	m-$NO_2{\cdot}C_6H_4$	22(20)	277—279 (d)	$C_{15}H_{16}O_4N_2S,HCl$	50·4	4·9	9·4	50·5	4·8	9·95
21	o-$OH{\cdot}C_6H_4$	7 [c]	225—227 (d)	$C_{15}H_{17}O_3NS,HCl$	—	—	11·1	—	—	10·8

* The percentage yields in the parentheses are those of the αβ-unsaturated sulphones.
[a] No β-amino-sulphone could be isolated. [b] No unsaturated sulphone could be isolated. Coumarins formed are described in Table 4. (d) M. p. with decomp.

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* *J.*, 1954, 1844, is now regarded as Part I.

solution of potassium permanganate. The excess of permanganate was then removed with sulphur dioxide, and the solution evaporated to dryness under reduced pressure. The residue was extracted with acetone and dried ($MgSO_4$), and the solvent removed. Ethyl-, propyl-, and butyl-sulphonylacetic acids solidified only after being kept in a vacuum-desiccator. Benzylsulphonylacetic acid was obtained by oxidising the alkylthio-acid in acetic acid with hydrogen peroxide (30%), concentrating the solution, and extracting it with boiling benzene. *Propylsulphonylacetic acid* melted at 41° (Found: C, 36·4; H, 6·0. $C_5H_{10}O_4S$ requires C, 36·15; H, 6·0%). It was hygroscopic. The other sulphonylacetic acids had m. p.s given in the literature (methyl: Mellander, *Svensk Kem. Tidskr.*, 1934, **46**, 99. Ethyl and benzyl: Rothstein, *J.*, 1937, 309. Butyl: Pomerantz and Connor, *J. Amer. Chem. Soc.*, 1939, **61**, 3139).

Condensation of alkylsulphonylacetic acids with aldehydes and ammonia. The condensation was effected as described for arylsulphonylacetic acids in Part I. The data relating to the β-amino-sulphone hydrochlorides, the bases, and the αβ-unsaturated sulphones are recorded in Tables 1—3 respectively.

2-*Benzylamino-2-phenylethyl methyl sulphone hydrochloride.* A mixture of methylsulphonylacetic acid (1·38 g.), benzaldehyde (1·06 g.), and benzylamine (1·07 g.) in acetic acid (2 c.c.) was

TABLE 2. β-*Amino-sulphones*, $R{\cdot}SO_2{\cdot}CH_2{\cdot}CHR'{\cdot}NH_2$ (*free bases; the nos. refer to the corresponding compounds in Table* 1).*

		Found (%)		Required (%)		Formula
No.	M. p.	C	H	C	H	
2	146—147°	49·25	5·45	49·4	5·35	$C_{10}H_{13}O_4NS$
3	77—79	43·1	5·8	42·9	5·6	$C_9H_{12}O_2NClS,H_2O$
7	72—73	45·3	5·9	45·2	6·0	$C_{10}H_{14}O_2NClS,H_2O$
9	101—102	46·6	5·6	46·5	5·4	$C_{10}H_{14}O_4N_2S$
11	44—45	50·7	6·5	50·5	6·1	$C_{11}H_{16}O_2NClS$
16	88—89	65·4	6·0	65·5	6·0	$C_{15}H_{17}O_2NS$
18	100—102	54·9	5·6	55·0	5·5	$C_{15}H_{16}O_2NClS,H_2O$
19	127—128	58·0	5·1	58·2	5·2	$C_{15}H_{16}O_2NClS$
21	153—154	61·9	5·4	61·9	5·8	$C_{15}H_{17}O_3NS$

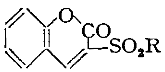
* Prepared from the hydrochlorides by means of aqueous ammonia and recrystallised from water or aqueous ethanol.

TABLE 3. αβ-*Unsaturated sulphones*, $R{\cdot}SO_2{\cdot}CH{:}CHR'$.

					Found (%)		Required (%)	
R	R′	M. p.	Solvent	Formula	C	H	C	H
Me	$3:4\text{-}(CH_2O_2)C_6H_3$	129—130°	MeOH	$C_{10}H_{10}O_4S$	52·7	4·2	53·1	4·4
Me	$o\text{-}C_6H_4Cl$	82—83	,,	$C_9H_9O_2ClS,H_2O$ *	46·4	4·5	46·15	4·7
Me	$m\text{-}NO_2{\cdot}C_6H_4$	130—132	,,	$C_9H_9O_4NS$	47·7	3·7	47·6	3·9
Et	Ph	66—67	H_2O	$C_{10}H_{12}O_2S,H_2O$ *	56·5	6·4	56·1	6·5
Et	$3:4\text{-}(CH_2O_2)C_6H_3$	80—81	,,	$C_{11}H_{12}O_4S$	55·3	4·9	55·0	5·0
Et	$o\text{-}NO_2{\cdot}C_6H_4$	89—90	,,	$C_{10}H_{11}O_4NS$	50·2	4·5	49·8	4·6
Et	$m\text{-}NO_2{\cdot}C_6H_4$	124—125	EtOH	$C_{10}H_{11}O_4NS$	50·1	4·5	49·8	4·6
Pr^n	$o\text{-}C_6H_4Cl$	76—77	MeOH	$C_{11}H_{13}O_2ClS,H_2O$ *	50·2	5·8	50·3	5·7
$PhCH_2$	Ph	144—145	CCl_4	$C_{15}H_{14}O_2S$	69·85	5·05	69·8	5·4
$PhCH_2$	$3:4\text{-}(CH_2O_2)C_6H_3$	150—151	EtOH	$C_{16}H_{14}O_4S$	63·6	4·7	63·6	4·6
$PhCH_2$	$o\text{-}C_6H_4Cl$	111—112	MeOH	$C_{15}H_{13}O_2ClS,H_2O$ *	58·2	4·7	58·0	4·8
$PhCH_2$	$p\text{-}C_6H_4Cl$	163—165	CCl_4	$C_{15}H_{13}O_2ClS,H_2O$ *	57·55	4·5	58·0	4·8
$PhCH_2$	$m\text{-}NO_2{\cdot}C_6H_4$	184—186	EtOH	$C_{15}H_{13}O_4NS$	59·4	4·3	59·4	4·3

* Since their analyses indicated water of crystallisation (which could not be removed by drying *in vacuo*) the possibility of these compounds' having the β-hydroxy-sulphone structure, $R{\cdot}SO_2{\cdot}CH_2{\cdot}CH(OH){\cdot}R'$, was considered. However, the compounds decolorised bromine in carbon tetrachloride and were recovered unchanged as hydrates after attempted acetylation or benzoylation. They also readily decolorised potassium permanganate in aqueous acetone.

TABLE 4. 3-*Alkylsulphonylcoumarins*,



R	Yield (%)	M. p.*	Formula	Found (%) C	Found (%) H	Required (%) C	Required (%) H
Me	6	184—185°	$C_{10}H_8O_4S$	53·1	3·9	53·6	3·6
Et	14	163—164	$C_{11}H_{10}O_4S$	55·1	4·3	55·5	4·2
Pr^n	12	140—141	$C_{12}H_{12}O_4S$	57·0	4·7	57·15	4·8
Bu^n	12	122—123	$C_{13}H_{14}O_4S$	58·35	5·4	58·6	5·3
CH_2Ph	20	161—162	$C_{16}H_{12}O_4S$	64·1	3·8	64·0	4·0

* Crystallised as needles from methanol.

refluxed for 10 min., cooled, and extracted with ether, and the extract was saturated with hydrogen chloride. The precipitated *hydrochloride* (0·3 g.), when crystallised from ethanol–ether, had m. p. 179—181° (Found : C, 55·7 ; H, 6·4 ; Cl^-, 10·5. $C_{16}H_{19}O_2NS,HCl,H_2O$ requires C, 55·9 ; H, 6·4 ; Cl^-, 10·3%). The filtrate obtained after removal of the above hydrochloride, yielded methyl ω-styryl sulphone (0·6 g.), m. p. 79—80° (from water). Truce, Simms, and Hill (*J. Amer. Chem. Soc.*, 1953, **75**, 5411) record m. p. 78—79°.

Benzyl 2-benzylamino-2-phenylethyl sulphone. By use of benzylsulphonylacetic acid (2·14 g.), benzaldehyde (1·06 g.), and benzylamine (1·07 g.) in acetic acid (2 c.c.), the condensation was effected as above. Addition of ether precipitated benzyl ω-styryl sulphone (0·6 g., see Table 3) which was filtered off, and from the filtrate the *hydrochloride* (0·35 g.) was obtained, having m. p. 187—189° (from ethanol–ether) (Found : Cl^-, 9·0. $C_{22}H_{23}O_2NS,HCl$ requires Cl^-, 8·8%). The *base* was obtained by treatment of the hydrochloride with aqueous ammonia, m. p. 108—109° (from ethanol–water) (Found: C, 69·2 ; H, 6·5. $C_{22}H_{23}O_2NS,H_2O$ requires C, 68·9 ; H, 6·5%).

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Chemistry of the Coprosma *Genus. Part X.* The Colouring Matters from* Coprosma rhamnoides.

By LINDSAY H. BRIGGS and A. R. TAYLOR.

[Reprint Order No. 6253.]

Coprosma rhamnoides (Oliver, " The Genus *Coprosma*," Bernice P. Bishop Museum Bull. 132, 1935) is a small shrub, 2—6 feet high, occurring throughout New Zealand to which it is endemic. As already reported (Part VIII, *J.*, 1954, 3940) the stem-bark contains asperuloside but no appreciable amount of colouring matter. The root-bark, however, is bright yellow.

Concentration of aqueous extracts of the root-bark afforded rutin. Chromatography of an acetone extract on magnesia gave a series of coloured bands from which rutin, anthragallol 1 : 2-dimethyl ether, and rubiadin 1-methyl ether were isolated.

Complete chromatography, based on a 1 : 1 mixture of magnesium carbonate and diatomaceous earth, gave more than three bands. Several of the lower bands, however, all gave the same product, rubiadin 1-methyl ether, and the material from single bands also gave two bands on rechromatography, from both of which, however, again only rubiadin 1-methyl ether was isolated.

It has been previously observed that other pure compounds in this series, such as 1-hydroxyanthraquinone, gave two bands on chromatography, from both of which the pure compound can be regenerated. Chromatography of hydroxyanthraquinones on magnesium oxide or carbonate columns is a phenomenon not necessarily of simple physical absorption with no colour change but mainly of chemical combination similar to ion-exchange, leading to differently coloured magnesium salts. The double bands in this case may be due to the two different types of absorption.

Experimental.—The analyses are by Dr. T. S. Ma, University of Otago.

The root-bark of *Coprosma rhamnoides* was collected in January from specimens growing at Piha. The ground, air-dried bark was first extracted with light petroleum (b. p. 50—65°) to remove wax and then with boiling water in a Soxhlet apparatus for 40 hr. Concentration of the extract to one-hundredth of the original volume afforded a single component (yield, *ca.* 10%), identified as rutin. Repeated crystallisation from water yielded minute, yellow needles, m. p. *ca.* 186°, decomp. above 200°, undepressed by authentic rutin. After drying at 100° the material was extremely hygroscopic (Found : C, 53·6, 53·35 ; H, 5·5, 5·5. Calc. for $C_{27}H_{30}O_{16}$: C, 53·4 ; H, 4·9%).

The glycoside was hydrolysed with 2% sulphuric acid solution at 100° for 7 hr. The insoluble aglycone crystallised from 60% acetic acid in rods, m. p. and mixed m. p. with quercetin, 316—316·5° (Found : C, 59·65 ; H, 3·8. Calc. for $C_{15}H_{10}O_7$: C, 59·6 ; H, 3·3%). The derived

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* Part IX, *J.*, 1954, 4182.

acetate had m. p. 191—192° (lit., m. p. 193·5°) and the pentamethyl ether m. p. 157—157·5° (lit., m. p. 151—152°).

The aqueous solution from the hydrolysis was neutralised on an ion-exchange column (Amberlite IRA-404) and concentrated to a small volume, and an aliquot part was treated in the usual way with phenylhydrazine. Microscopical examination of the osazones formed showed the presence of two types of crystal, long thin rods and curved needles, characteristic of glucosazone and rhamnosazone respectively (Hassid and McReady, *Ind. Eng. Chem. Anal.*, 1942, **14**, 883). Paper chromatography of a drop of the solution, with butanol–pyridine–water (Hough, Jones, and Wadman, *J.*, 1950, 1702) for 28 hr., and aniline hydrogen phthalate as spray, afforded two spots, identified with glucose and rhamnose from control experiments.

Chromatographic separation. The bark from the aqueous extraction was dried and extracted to completion with acetone. Rubiadin 1-methyl ether separated from the extract on cooling. Separation was best achieved by chromatography on a 1 : 1 mixture of magnesium carbonate and diatomaceous earth which gave even bands throughout. The material recovered from the bands by treatment with dilute hydrochloric acid was then rechromatographed on smaller columns.

The top band afforded rutin, m. p. and mixed m. p. 186°, after crystallisation from water. The material from the second major, dark orange band crystallised from alcohol in rhombohedral plates, m. p. and mixed m. p. with anthragallol 1 : 2-dimethyl ether, 238°. The colour reactions also agreed with this identification.

The lower bands varied in colour through yellow to brown and exhibited tailing with pinkish tints. Rechromatography of apparently single bands also afforded bands of similar colour with marked tailing. Isolation of the anthraquinone compounds from these bands, however, failed to yield any compound other than rubiadin 1-methyl ether, which was obtained as yellow needles, m. p. and mixed m. p. 290°, after crystallisation from glacial acetic acid (Found: C, 71·1; H, 4·8. Calc. for $C_{16}H_{12}O_4$: C, 71·6; H, 4·5%). The colour reactions, the acetate, m. p. and mixed m. p. 175—176°, and the fully methylated ether, m. p. and mixed m. p. 159—161° (cf. Part I, *J.*, 1948, 564), confirmed the identification.

We are indebted to the Chemical Society, the Australian and New Zealand Association for the Advancement of Science and the Research Grants Committee of the University of New Zealand for grants, to Messrs. Rohm and Haas Company, Philadelphia, for the gift of chemicals, and to Mr. D. E. Cooper, M.Sc., for practical assistance.

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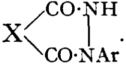
N′-2 : 4-*Dinitrophenyl*-NN-*phthaloylhydrazine.*

By M. Z. BARAKAT, S. K. SHEHAB, and M. M. EL-SADR.

[Reprint Order No. 6268.]

2 : 4-DINITROPHENYLHYDRAZINE was reported by Cerezo and Olay (*Anales Fís. Quím.*, 1934, **32**, 1090) to condense with dibasic acids, *e.g.*, succinic or phthalic acid, to give *NN*- or *NN′*-derivatives, $X < [CO]_2 > N·NHAr$ or  $X\left\langle\begin{matrix}CO·NH\\|\\CO·NAr\end{matrix}\right.$. This reaction with phthalic acid is rapidly effected in boiling dioxan in presence of phosphoric oxide or zinc chloride, the yield being 50%.

With nitrous oxides in acetic acid (Hötte, *J. prakt. Chem.*, 1887, **35**, 265) or with fuming nitric acid in acetic–sulphuric acid *N′*-phenyl-*NN*-phthaloylhydrazine gives a dinitro-derivative; Hötte (*loc. cit.*) located one nitro-group on nitrogen, and Ohta (*J. Pharm. Soc. Japan*, 1944, **64**, No. 10A, 49) placed the other as in a *p*-nitrophenyl group. The product is, however, identical (mixed m .p.) with *N′*-2 : 4-dinitrophenyl-*NN*-phthaloylhydrazine prepared as above.

Condensation as above gives *ca.* 55% yields of various imides and hydrazides. We have thus prepared: *N*-phenyl-, *N*-*p*-nitrophenyl-, *N*-*p*-tolyl-, and *N*-1-naphthyl-succinimide; *N′*-phenyl- and *N′*-2 : 4-dinitrophenyl-*NN*-succinylhydrazine; and the corresponding phthaloyl derivatives. Acetanilide, benzanilide, and benzo-*m*-toluidide were similarly prepared.

Experimental.—Preparation of N'*-phenyl-*NN*-phthaloylhydrazine.* Phthalic acid (1·66 g., 0·01 mole), phenylhydrazine (1·08 g., 0·01 mole), and anhydrous zinc chloride (3 g.) in dioxan (20 ml.) were refluxed for 2 hr., then allowed to cool and poured on crushed ice. A yellow solid separated which was filtered off and recrystallised either from hot ethyl alcohol and a few drops of water, or from acetone, giving uniform yellow prisms, m. p. 184° (55%).

Nitration of N'*-phenyl-*NN*-phthaloylhydrazine.* The hydrazide (0·8 g.) was dissolved in hot glacial acetic acid (6 ml.). To the cold solution concentrated sulphuric acid (2 ml.) was added drop by drop with shaking, then similarly nitric acid (*d* 1·45; 2 ml.). After 10 min. the mixture was poured on crushed ice. The yellowish-orange product was filtered off and recrystallised from aqueous alcohol or glacial acetic acid (charcoal), giving yellow crystals, m. p. 270—272° (decomp.) (0·58 g.).

Preparation of N'*-2 : 4-dinitrophenyl-*NN*-phthaloylhydrazine.* Phthalic acid (1·66 g., 0·01 mole), 2 : 4-dinitrophenylhydrazine (1·98 g., 0·01 mole), and anhydrous zinc chloride (3 g.) in dioxan (20 ml.) were refluxed for 2 hr., allowed to cool, and poured on crushed ice. The solid product was filtered off and recrystallised from boiling glacial acetic acid (charcoal). Yellow crystals (50%) were obtained, having m. p. 272—274° (decomp.) alone or mixed with the preceding product.

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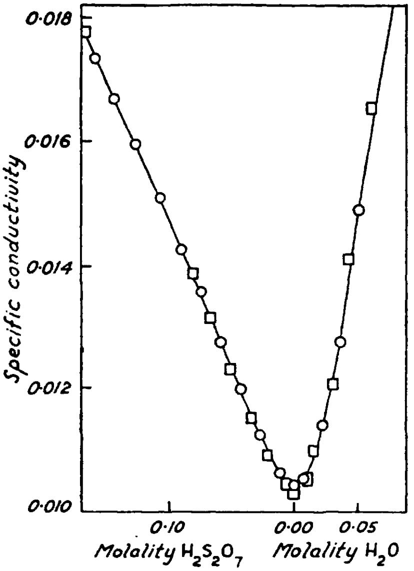
The Electrical Conductivity of Sulphuric Acid.

By G. HETHERINGTON, D. R. HUB, M. J. NICHOLS, and P. L. ROBINSON.

[Reprint Order No. 6285.]

BEFORE making measurements of the electrical conductivity of solutions in sulphuric acid (Hetherington, Nichols, and Robinson, *J.*, in the press), it was desirable to repeat those made on the system water–sulphur trioxide in the equimolecular region: first, because the specific conductivities reported within the last 25 years differ by 0·00027 ohm^{-1} cm.$^{-1}$; secondly, because the determinations provide a convenient check on the technique we intended to use; and, lastly, because the measurement of conductivity furnishes the most convenient and accurate means of characterising our solvent. This note simply deals with the preparation of the solutions and presents the results which, when considered in relation to the published figures, are thought to narrow the limits within which the conductivity of



Some specific conductivities of the water–sulphur trioxide system.

○ Present authors.
□ Gillespie and Wasif.

sulphuric acid lies. The cell used and the method of measurement will be described in a later communication.

Since Kohlrausch (*Wied. Ann.*, 1882, **17**, 69) and Knietsch (*Ber.*, 1901, **34**, 4107) sought to establish the composition corresponding to minimum conductivity in the system H_2O-SO_3—recently shown by Kunzler and Giauque (*J. Amer. Chem. Soc.*, 1952, **74**, 804) to be 99·996 ± 0·001% (by wt.) sulphuric acid at 10·37°—six determinations of the specific conductivity of sulphuric acid at 25° have appeared, as follows :

	ohm^{-1} cm.$^{-1}$
(i) Hantzsch (*Z. physikal. Chem.*, 1907, **61**, 257)	0·0098
(ii) Lichty (*J. Amer. Chem. Soc.*, 1908, **30**, 1834)	0·01041
(iii) Bergius (*Z. physikal. Chem.*, 1910, **72**, 338)	0·0097
(iv) Ussanowitsch, Sumarakowa, and Udowenko (*Acta Phys. Chim. U.R.S.S.*, 1939, **11**, 505)	0·0106
(v) Reinhardt (*J. Amer. Chem. Soc.*, 1950, **72**, 3359)	0·0108
(vi) Gillespie and Wasif (*J.*, 1953, 204)	0·01033

To these we add a seventh, *viz.*, 0·01045 ohm^{-1} cm.$^{-1}$.

Our value is almost identical with (ii) and only 0·00012 ohm^{-1} cm.$^{-1}$ above the last determination (vi). A large-scale plot of conductivities against composition, over the range 0·2 mole H_2O to 0·4 mole $H_2S_2O_7$ which we covered, shows that our points lie very close to those of Gillespie and Wasif (*loc. cit.*), except at the minimum value, where they are a little higher. These authors have given reasons for doubting the accuracy of determinations (i), (iv), and (v) that seem well founded, and (iii) is very low. Thus we are left with determinations (ii), (vi), and our own which, from their concordance, suggest that the mean, 0·01040 ohm^{-1} cm.$^{-1}$, is very close to the conductivity of absolute sulphuric acid at 25°.

Experimental.—The starting materials were dilute oleum and water. The former was prepared by passing sulphur trioxide vapour into 98% " AnalaR " sulphuric acid under reduced pressure at room temperature. The latter was laboratory distilled water which, immediately before use, was redistilled from a little potassium permanganate and sodium hydroxide, precaution being taken to avoid contamination by spray.

A weighed amount of oleum was successively diluted with weighed amounts of water, and the specific conductivity was measured at each stage of the dilution. The precise composition of the oleum was calculated at the end of the series, it being assumed that the point of minimum conductivity corresponded to a composition represented by H_2SO_4.

The specific conductivity of the water–sulphur trioxide system about the region of sulphuric acid at 25° in ohms^{-1} cm.$^{-1}$.

Molality $H_2S_2O_7$	$10^2\,\kappa$	Molality $H_2S_2O_7$	$10^2\,\kappa$	Molality $H_2S_2O_7$	$10^2\,\kappa$	Molality H_2O	$10^2\,\kappa$
0·3059	2·233	0·0977	1·469	0·0349	1·161	0·0000	1·045
0·2971	2·210	0·0894	1·424	0·0272	1·124	0·0019	1·046
0·2729	2·136	0·0830	1·397	0·0193	1·091	0·0072	1·054
0·2400	2·031	0·0798	1·385	0·0113	1·064	0·0149	1·087
0·2004	1·893	0·0769	1·371	0·0000	1·045	0·0226	1·141
0·1591	1·735	0·0740	1·359			0·0376	1·298
0·1436	1·670	0·0661	1·318			0·0528	1·490
0·1263	1·598	0·0580	1·279			0·0846	1·941
0·1155	1·549	0·0502	1·240			0·1220	2·452
0·1066	1·509	0·0427	1·201			0·1608	2·950

This work was carried out during the tenure of a Salters' Fellowship (G. H.) and a D.S.I.R. maintenance grant (D. R. H.).

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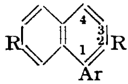
1-*Phenylnaphthalenes.*

By F. G. Baddar, H. A. Fahim, and A. M. Fleifel.

[Reprint Order No. 6338.]

Contrary to Mitter and De (*J. Indian Chem. Soc.*, 1939, **16**, 199) the condensation of methylsuccinic anhydride with anisole in presence of aluminium chloride and nitrobenzene gave a mixture of β-*p*-methoxybenzoyl-α-methylpropionic acid and β-*p*-methoxybenzoylbutyric acid in the ratio of 13 : 1, respectively. The ratio of the β-methyl acid increased enormously when nitrobenzene was replaced by *s*-tetrachloroethane (cf. Baddar, Fahim, and Fleifel, *J.*, 1955, 2199). 7-Methoxy-2-methyl-1-tetralone gave with *o*-methoxyphenylmagnesium iodide (20 hours' refluxing), 3 : 4-dihydro-7-methoxy-1-*o*-methoxyphenyl-2-methylnaphthalene, which was dehydrogenated with selenium to 7-methoxy-1-*o*-methoxyphenyl-2-methylnaphthalene (I*a*). 2 : 7-Dimethyl-1-tetralone was similarly condensed with phenyl-, *p*-tolyl-, and *m*-tolyl-magnesium halide to give tertiary alcohols, which were dehydrated, then dehydrogenated with selenium to the naphthalenes (I*b*, *c*, and *d*), respectively. The low reactivity of the above tetralones towards Grignard reagents and the difficulty in dehydrating the resulting tertiary alcohols may be attributed to the $+I$ effect of the 2-methyl group.



(I*a*) Ar = C_6H_4·OMe-*o*, R' = Me, R = OMe
(I*b*) Ar = Ph, R' = R = Me
(I*c*) Ar = C_6H_4·Me-*p*, R = R' = Me
(I*d*) Ar = C_6H_4·Me-*m*, R = R' = Me

2-Methoxy-1-*o*-methoxyphenylnaphthalene (I; R = H, R' = OMe, Ar = C_6H_4·OMe-*o*) was prepared by decarboxylation of 1-(5-carboxy-2-methoxyphenyl)-2-methoxynaphthalene.

Experimental.—Condensation of methylsuccinic anhydride with anisole. The product (15 g., m. p. 110—136°) from methylsuccinic anhydride (11·4 g.), anisole (10 g.), and aluminium chloride (26·7 g.) in nitrobenzene (70 ml.) [cf. Mitter and De (*loc. cit.*)] was crystallised from glacial acetic acid, to give β-*p*-methoxybenzoyl-α-methylpropionic acid, m. p. 145—146°. Mitter and De (*loc. cit.*), and Mehta, Bokil, and Nargund (*J. Univ. Bombay*, 1943, **12**, *A*, 64) gave m. p. 144° and 141°, respectively.

The original acetic acid mother-liquor was evaporated in a vacuum to dryness, and the remaining oil (1·2 g.) was converted into β-*p*-methoxybenzoylbutyric acid semicarbazone, m. p. 179—180° (from ethanol), depressed to 145—157° on admixture with the semicarbazone of the α-methyl acid. Dhekne and Bhide (*J. Indian Chem. Soc.*, 1951, **28**, 504) gave m. p. 186°.

When nitrobenzene was replaced by *s*-tetrachloroethane the ratio of the α- to the β-methyl acid was 3 : 1. Both acids gave anisic acid on oxidation with 10% sodium hypobromite solution (cf. Baddar, Fahim, and Fleifel, *loc. cit.*).

3 : 4-*Dihydro*-7-*methoxy*-1-o-*methoxyphenyl*-2-*methylnaphthalene*. A solution of 2-methyl-7-methoxy-1-tetralone (3·8 g., 1 mol.) in dry thiophen-free benzene (30 ml.) was gradually added to an ethereal solution of *o*-methoxyphenylmagnesium iodide (from *o*-iodoanisole, 14·1 g., 3 mols.). Ether was driven off, and the mixture refluxed for 20 hr. and worked up as usual (cf. Baddar and El-Assal, *J.*, 1951, 1844). The product, b. p. 186—190°/6 mm., gave the *dihydronaphthalene* (56%), m. p. 57—58° (from ethanol) (Found : C, 81·4; H, 6·8; OMe, 23·5. $C_{19}H_{20}O_2$ requires C, 81·4; H, 7·1; OMe, 22·1%).

7-*Methoxy*-1-o-*methoxyphenyl*-2-*methylnaphthalene* (I*a*). This was prepared by heating the dihydro-compound with selenium powder at 330—340° for 3 hr. The *product* (40%) had b. p. 225—235°/10 mm., m. p. 68—69° (from dilute methanol) (Found : C, 81·0; H, 6·8; OMe, 24·4. $C_{19}H_{18}O_2$ requires C, 82·0; H, 6·5; OMe, 22·3%).

3 : 4-*Dihydro*-2 : 7-*dimethyl*-1-*phenylnaphthalene*.—2 : 7-Dimethyl-1-tetralone was prepared in 84% yield by heating the corresponding butyric acid with 85% sulphuric acid for 1 hr. on the water-bath (cf. Mayer and Stamm, *Ber.*, 1923, **56**, 1424; Baker, MacOmie, and Warburton, *J.*, 1952, 2991). When this tetralone (3·5 g., 1 mol.) was condensed with phenylmagnesium iodide (3 mols.) as previously mentioned, it gave 3 : 4-*dihydro*-2 : 7-*dimethyl*-1-*phenylnaphthalene* (53%), b. p. 182—184°/7 mm., $n_D^{30} > 1·7$ (Found : C, 91·6; H, 7·6. $C_{18}H_{18}$ requires C, 92·3; H, 7·7%).

2 : 7-*Dimethyl*-1-*phenylnaphthalene* (I*b*). This *hydrocarbon* was obtained by the dehydrogenation of the above dihydro-compound with selenium; it had b. p. 230—235°/10 mm., n_D^{30} 1·657 (Found : C, 92·7; H, 7·1. $C_{18}H_{16}$ requires C, 93·1; H, 6·9%). It failed to give either a solid mononitro-derivative or a stable adduct with 2 : 4 : 7-trinitrofluorenone or styphnic acid.

3 : 4-*Dihydro*-2 : 7-*dimethyl*-1-p-*tolylnaphthalene*. This was obtained as usual in 66% yield from 2 : 7-dimethyl-1-tetralone (3·5 g., 1 mol.) and *p*-tolylmagnesium iodide (3 mols.). The compound had b. p. 190—192°/7 mm., n_D^{30} >1·7 (Found : C, 89·6; H, 8·0. Calc. for $C_{19}H_{20}$: C, 91·9; H, 8·1%). It contained 0·07% of active hydrogen even after dehydration with potassium hydrogen sulphate.

2 : 7-*Dimethyl*-1-p-*tolylnaphthalene* (I*c*) was prepared by the dehydrogenation of the dihydro-compound with selenium, and had b. p. 215—220°/10 mm., n_D^{30} >1·7 (Found : C, 91·9; H, 7·4. $C_{19}H_{18}$ requires C, 92·7; H, 7·3%).

3 : 4-Dihydro-2 : 7-dimethyl-1-*m*-tolylnaphthalene, obtained in 40% from 2 : 7-dimethyl-1-tetralone and *m*-tolylmagnesium bromide, had b. p. 166—170°/7 mm., n_D^{30} 1·5951 (Found : C, 90·0; H, 7·9%). The low carbon content may be due to incomplete dehydration of the alcohol. It gave 2 : 7-*dimethyl*-1-m-*tolylnaphthalene* (I*d*), b. p. 220—230°/7 mm., n_D^{30} >1·7, in 40% yield from the dihydro-compound as usual (Found : C, 91·6; H, 7·2%).

1-*Iodo*-2-*methoxynaphthalene*. This was obtained in 88% by iodination of 2-methoxynaphthalene (5 g., 1 mol.) with powdered iodine (8·4 g., 1·1 mols.) and yellow mercuric oxide (7·2 g., 1 mol.) in carbon tetrachloride (100 ml.) and acetic anhydride (3 ml.) at room temperature; it had m. p. 87—88°. Ray and Moomaw (*J. Amer. Chem. Soc.*, 1933, **55**, 3833) gave m. p. 88°.

1-(5-*Carboxy*-2-*methoxyphenyl*)-2-*methoxynaphthalene*. Methyl 3-iodo-4-methoxybenzoate (7·4 g., 1 mol.) was condensed with 1-iodo-2-methoxynaphthalene (7·2 g., 1 mol.) in presence of copper bronze (9·5 g.) at 230—235° for 5·5 hr. The product was worked up as usual, and the benzene-soluble *acid* formed needles, m. p. 243—244° (from methanol) (Found : C, 73·5; H, 5·4; OMe, 20·3. $C_{19}H_{16}O_4$ requires C, 74·0; H, 5·2; OMe, 20·1%). The *methyl ester* had m. p. 179—180° (from methanol) (Found : C, 74·8; H, 5·5. $C_{20}H_{18}O_4$ requires C, 74·5; H, 5·6%).

The benzene-insoluble acid was methylated, to give *dimethyl* 2 : 2′-*dimethoxydiphenyl*-5 : 5′-*dicarboxylate*, m. p. 169—170° (from methanol), depressed on admixture with the above ester (Found : C, 65·7; H, 5·8; OMe, 36·6. $C_{18}H_{18}O_6$ requires C, 65·5; H, 5·5; OMe, 37·6%).

2-*Methoxy*-1-o-*methoxyphenylnaphthalene*. This *ether* was prepared by heating the above acid (0·5 g.) with copper bronze (0·4 g.) in quinoline (5 ml.) at 210° for 2 hr. The product, b. p. 220—230°/6 mm. (0·25 g.), formed needles, m. p. 97—98°, from methanol (Found : C, 81·0; H, 6·1; OMe, 24·8. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·1; OMe, 23·5%).

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The Mechanism of the Hydrolysis of Acetyl Chloride.

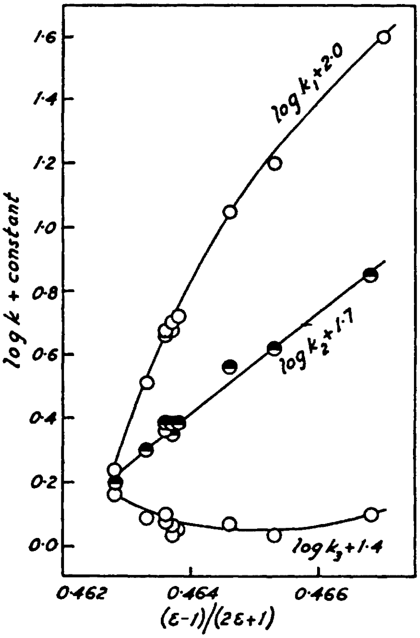
By V. GOLD and J. HILTON.

[Reprint Order No. 6342.]

IN a recent note Zimmerman and Yuan (*J. Amer. Chem. Soc.*, 1955, **77**, 332) reported measurements of the rate of hydrolysis of acetyl chloride in acetone containing small amounts of water. The velocity was found to be roughly proportional to the square of the water concentration, and the authors concluded from this that the reaction was termolecular, in agreement with views previously expressed by Swain (*ibid.*, 1948, **70**, 1124) and by Archer and Hudson (*J.*, 1950, 3259). Recently we tentatively proposed a bimolecular mechanism for this reaction in aqueous solution (*J.*, 1955, 838). We now show that Zimmerman and Yuan's results also support a bimolecular mechanism (for the hydrolysis in acetone–water) and that they cannot be regarded as unambiguous evidence for a termolecular mechanism.

It was pointed out by Bateman, Cooper, and Hughes (*J.*, 1940, 917; Hughes, *Trans. Faraday Soc.*, 1941, **37**, 603) that the apparent order of a reaction with respect to water in acetone solution need not reflect the molecularity of the reaction with respect to water and, for the same reason, we do not accept the validity of the conclusions drawn by Zimmerman and Yuan.

The inadequacy of their procedure can be regarded as being due to the large change in solvent properties which is caused by the addition of small amounts of water to acetone. This change is shown, for example, by the dielectric constant (Åkerlöf, *J. Amer. Chem. Soc.*, 1932, **54**, 4132). It is known that the rates of heterolytic reactions in mixed solvents vary with the composition of the solvent in a manner which is consistent with the hypothesis that the influence of solvent variation on the reaction rate is largely due to the change in the dielectric constant (Glasstone, Laidler, and Eyring, " The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, 1941, Chapter VIII). Hydrolysis reactions in which water is a reactant involve a separation of charges in the transition state—whatever the molecularity of the reaction (Gold, *Trans. Faraday Soc.*, 1948, **44**, 506)—and the rate coefficients are therefore expected to increase with the dielectric constant (ε) of the medium. If the simplest electrostatic theory can be applied to this type of reaction, log *k* should be a linear function of $(\varepsilon - 1)/(2\varepsilon + 1)$ (cf. Gold, Hilton, and Jefferson, *J.*, 1954, 2756). This treatment has been applied to rate measurements for a number of heterolytic reactions and the order of magnitude of the dielectric-constant dependence to be expected is therefore known (Cowan, McCabe, and Warner, *J. Amer. Chem. Soc.*, 1950, **72**, 1194).



We have accordingly examined the variation of the first-, second-, and third-order rate coefficients, calculated from Zimmerman and Yuan's data, as a function of dielectric constant. A plot of the logarithms of the three rate coefficients against $(\varepsilon - 1)/(2\varepsilon + 1)$ (a monotonic function of ε over the range of interest) is shown in the Figure. The dielectric constants used were derived by interpolation from Åkerlöf's measurements (*loc. cit.*) and the estimated uncertainties in this interpolation and of the experimental rate constants are indicated in the Figure by the size of the circles. It is found that the first- and the second-order rate coefficients show qualitatively the expected kind of dependence on dielectric constant. If linearity of the plot is taken as a criterion of mechanism (Archer and Hudson, *loc. cit.*; cf. Gold, Hilton, and Jefferson, *loc. cit.*) the bimolecular mechanism appears to be the most satisfactory. As there are other reasons why a unimolecular mechanism seems unlikely for this reaction in wet acetone, we conclude that, under these conditions, the hydrolysis of acetyl chloride is indeed bimolecular and that it is an example of hydrolysis for which the simple electrostatic treatment of dipole–dipole reactions is a good approximation.

Since there are no reactions of this kind for which a termolecular mechanism has been established beyond reasonable doubt, it is impossible to state categorically that the observed dependence of the third-order rate coefficient on dielectric constant might not be typical of the behaviour of termolecular rate coefficients. However, since reasonable models of a termolecular transition state still involve a structure of greater polarity than that of the reactant molecules, a termolecular rate coefficient is expected to increase with dielectric constant. We cannot, by any simple electrostatic treatment, account for the minimum in the curve of log k_3. In the light of these considerations, the termolecular mechanism appears to be the least satisfactory alternative considered.

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Prodigiosin.

By E. N. Morgan and (Miss) E. M. Tanner.

[Reprint Order No. 6383.]

Few details of the physical properties of purified prodigiosin have been recorded. Wrede and Hettche (*Ber.*, 1929, **62**, 2678) describe the free base as an amorphous mass, sintering between 70° and 80°. The perchlorate has a recorded m. p. of 228° (sintering at 226°). Hubbard and Rimington (*Biochem. J.*, 1950, **46**, 220) investigated the ultraviolet absorption of prodigiosin and of the perchlorate.

During the preparation of a sample for biological testing the purified base was obtained in lustrous, square pyramids, m. p. 151—152°, which were dark red with a green reflex. The ultraviolet absorption properties of the base and the infrared properties of both the base and the perchlorate are recorded below. The perchlorate had m. p. 227—229° undepressed by a sample of authentic prodigiosin perchlorate.

The essential features of the ultraviolet and visible spectrum of prodigiosin recorded by Hubbard and Rimington (*loc. cit.*) are confirmed by the results given below, except for the absence of bands around 250 mμ and the presence of several smaller bands. The striking change in colour from deep red in acid solution to the orange-yellow in alkaline solution is revealed in the intense narrow band at 541 mμ in the former and the broad, less intense band, centred at 468 mμ, in the latter. Neutral solutions (pH 7·4) in alcohol show the orange-yellow colour and the spectrum of alkaline solutions, together with a small band at 540 mμ indicating the presence of a small quantity of the red chromophore.

Experimental.—Crude prodigiosin, prepared by Commercial Solvents Corp. and made available to us through the courtesy of Dr. E. F. Elslager of Parke, Davis & Company, Detroit, U.S.A., was kept overnight at room temperature in methanol. After filtration, the dry pigment (2 g.) was dissolved in light petroleum (b. p. 60—80°) and chromatographed on an alumina column. The main scarlet band was removed mechanically and extracted with cold methanol. After concentration, the chilled extract deposited the pigment (1 g.). Recrystallisation from light petroleum (b. p. 60—80°) gave (slowly) square pyramids, m. p. 151—152° (Found: C, 73·9; H, 7·7; O, 5·5; N, 13·0. $C_{20}H_{25}ON_3$ requires C, 74·3; H, 7·8; O, 5·0; N, 13·0%).

Ultraviolet absorption in EtOH: (*a*) pH 7·4, max. at 225·5, 288·5, 337·0, 471·0, and 539·0 mμ (ε 10,810, 9820, 7590, 41,600, and 17,240 respectively); (*b*) pH 11, max. at 257·0, 281·0, 335·5, and 468·5 mμ (ε 7950, 9520, 7860, and 42,400 respectively); (*c*) pH 2·9, max. at 216·0, 296·0, 371·0, and 541·0 mμ (ε 8660, 12,220, 7750, and 132,200 respectively) and inflections at 275·0, 382·0, and 510·0 mμ (ε 6440, 7240, and 54,400 respectively).

Infrared spectrum (KBr discs): max. at 3270, 3235, 3070, 2895, 2835, 1622, 1578, 1557, 1543, 1458, 1430, 1373, 1360, 1336, 1277, 1253, 1198, 1185, 1144, 1136, 1115, 1078, 1054, 1030, 998, 957, 926, 907, 890, 844, 821, 806, 782, 767, 739, and 727 cm.$^{-1}$.

The perchlorate (Found: N, 9·9. Calc. for $C_{20}H_{25}ON_3,HClO_4$: N, 9·9%) (yield 80%) was undepressed on admixture with a sample of prodigiosin perchlorate originally prepared by Prof. Wrede, and supplied to us through the courtesy of Prof. C. Rimington, University College Hospital Medical School, London, to whom we express our gratitude.

Infrared spectrum (KBr discs): max. at 3310, 3240, 3085, 2910, 2845, 1622, 1605, 1517, 1455, 1465, 1379, 1337, 1315, 1297, 1285, 1264, 1242, 1202, 1150, 1129, 1119, 1094, 1080, 1066, 1043, 1012, 991, 962, 918, 885, 870, 862, 836, 822, 797, and 727 cm.$^{-1}$.

The ultraviolet absorption measurements were made on a Unicam SP500 Spectrophotometer, and the infrared spectra were obtained on a Grubb-Parsons S3A Spectrometer.

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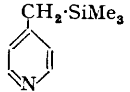
Organosilicon Compounds. Part XV. Derivatives of α- and γ-Picoline.*

By C. Eaborn and R. A. Shaw.

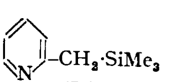
[Reprint Order No. 6387.]

In continuation of our study of organosilicon compounds derived by substitution at a reactive C–H bond (cf. *J.*, 1955, 1420), we have prepared 4- and 2-(trimethylsilylmethyl)-pyridine (I) and (II), and α-[bis(trimethylsilyl)methyl]pyridine (III). As expected from the acidities of the ω-hydrogen atoms of the parent picolines, the C–Si bonds are reactive in all three compounds, but distinctly least so in the disubstituted compound (III).

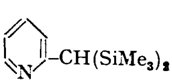
The 4-derivative (I) was completely cleaved (to γ-picoline and hexamethyldisiloxane) in 48 hr. by boiling aqueous ethanol; the 2-derivative (II) was more slowly cleaved, while compound (III) was little changed in 20 hr. The same order of reactivity, (I) > (II) ≫ (III), was found in alkaline and acidic cleavage. With 90% ethanol–water containing 5% of potassium hydroxide the base (I) was completely cleaved in ¼ hr. and the base (II) in 8 hr. at room temperature, while the disubstituted base (III) was only very slowly attacked at room temperature but was completely cleaved in 1 hr. at the boiling point. Aqueous 2N-hydrochloric acid at room temperature cleaved the base (I) in less than ½ hr., base (II) in 1½ hr., and base (III) in 16 hr.



(I)



(II)



(III)

If possible steric effects are neglected the greater reactivity in neutral and alkaline cleavage of the 4-derivative (I) compared with the 2-derivative (II) implies that the reactivity of the ω-hydrogen atoms is greater in γ- than in α-picoline (but see Bergstrom, *Chem. Rev.*, 1944, **35**, 85). The lower reactivity of the base (III) probably results from a combination of the electron release of the trimethylsilyl group and the steric hindrance it provides to solvation, both of which would lower the stability of the anion $2\text{-Me}_3\text{Si}\cdot\bar{\text{C}}\text{H}\cdot\text{C}_5\text{H}_4\text{N}$ and hence decrease the tendency of the ion to be formed in the cleavage reaction.

The easy acidic cleavage of the C–Si bond in the compounds no doubt follows protonation of the nitrogen atom, to give a positively charged entity in which the silicon atom is very susceptible to attack by the solvent. This is confirmed by the instability of the C–Si bonds of the picrates of bases (I) and (II), both of which are rapidly cleaved by ethanol. The lower reactivity of the disubstituted derivative (III) is again probably due to steric hindrance to solvation of the ion, $\text{Me}_3\text{Si}\cdot\bar{\text{C}}\text{H}\cdot\text{C}_5\text{H}_4\overset{+}{\text{N}}\text{H}$, formed in the cleavage. Steric hindrance also accounts for the inability of base (III) to form a picrate in dry ether, under which conditions bases (I) and (II) readily form such salts. An attempt to prepare the hydrochloride of the 4-derivative (I) by passing dry hydrogen chloride into its anhydrous ethereal solution led to cleavage with immediate precipitation of γ-picoline hydrochloride.

Replacement of the ω-hydrogen atoms of α-picoline by trimethylsilyl groups causes successive increase in the wavelength and the intensity of the main near-ultraviolet absorption maximum, while replacement of an ω-hydrogen atom of γ-picoline has little effect on the wavelength but decreases the intensity. The effects of the trimethylsilyl-methyl group on the absorption of pyridine are in the same direction as, but are greater than, those of a similarly placed methyl group (Herington, *Discuss. Faraday Soc.*, 1950, **9**, 26).

Experimental.—*2-(Trimethylsilylmethyl)pyridine and 2-[bis(trimethylsilyl)methyl]pyridine.* α-Picoline (102 g., 1·10 mole) in ether (100 ml.) was added to potassamide [prepared from

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* Part XIV, *J.*, 1955, 2517.

potassium (41 g., 1·05 g.-atoms)] in liquid ammonia (1 l.). The ammonia was replaced by ether (750 ml.), and chlorotrimethylsilane (120 g., 1·10 moles) in ether (100 ml.) was added with stirring during 1½ hr. at such a rate as to keep the solution boiling gently. The mixture was boiled under reflux for 4 hr. and set aside overnight. Water was added and the ethereal layer was washed with water and then dried (Na_2SO_4). After removal of the ether the residue was fractionated in a glass-helices column (*ca.* 15 plates) to give α-picoline (29 g.), 2-(*trimethylsilylmethyl*)*pyridine* (II) (10·4 g., 6·7%), b. p. 191—192°, n_D^{25} 1·4866 (Found : C, 65·6; H, 9·3; N, 8·6; Si, 16·6. $C_9H_{15}NSi$ requires C, 65·4; H, 9·15; N, 8·5; Si, 17·0%), and 2-[*bis*(*trimethylsilyl*)*methyl*]*pyridine* (III) (16·4 g., 13·3%), b. p. 237—237·5°, n_D^{25} 1·4950 (Found : C, 60·6; H, 9·9. $C_{12}H_{23}NSi$ requires C, 60·7; H, 9·8%).

4-(*Trimethylsilylmethyl*)*pyridine*. To γ-picolylpotassium [prepared as for the α-analogue from potassium (60 g., 1·53 g.-atom), liquid ammonia, and γ-picoline (170 g., 1·83 moles)] in ether (1 l.), chlorotrimethylsilane (180 g., 1·62 mole) in ether (250 ml.) was added with stirring during 1½ hr. The mixture was boiled for 3 hr. and set aside overnight. By a procedure similar to that used for the α-compounds, but with fractionation in a spinning-band column there were obtained γ-picoline (98 g.) and 4-(*trimethylsilylmethyl*)*pyridine* (II) (26 g., 10·3%), b. p. 73—74°/4·5 mm., n_D^{24} 1·5000 (Found : C, 65·25; H, 9·15. $C_9H_{15}NSi$ requires C, 65·4; H, 9·15%), a colourless liquid which became yellow on exposure to air. A higher-boiling residue decomposed when attempts were made to fractionate it.

Picrates. Bases (I) and (II) with picric acid in ether gave, respectively, precipitates of 2-, m. p. 124° (Found : C, 45·9; H, 4·7; N, 14·0. $C_{15}H_{18}O_7N_4Si$ requires C, 45·7; H, 4·6; N, 14·2%), and 4-(*trimethylsilylmethyl*)*pyridine picrate*, m. p. 120° (Found : C, 45·9; H, 4·7%), in 75% yield. When these picrates were briefly boiled with ethanol and the solution was cooled, only 2-picoline picrate, m. p. and mixed m. p. 168°, and γ-picoline picrate, m. p. and mixed m. p. 165—166°, respectively, separated.

No precipitate was obtained in 2 months from a solution of the base (III) (0·98 g.) and picric acid (1·02 g.) in ether (175 ml.).

Neutral and alkaline cleavage. The course of these cleavages was followed by adding samples of the reaction mixture to water, in which the organosilylpicolines and hexamethyldisiloxane are insoluble but the parent picolines are soluble. The liquid which separated was washed with water and its refractive index was determined.

Boiling with 95% ethanol–water gave the following results :

Compound (I)		Compound (II)		Compound (III)	
Time (hr.)	n_D^{23}	Time (hr.)	n_D^{21}	Time (hr.)	n_D^{21}
0	1·5000 [(I)]	0	1·4873 [(II)]	0	1·4966 [(III)]
4	1·4220	2	1·4634	8	1·4924
7	1·4140	8	1·4315	20	1·4900
22	1·3920	24	1·4110		
48	1·3772 [$(Me_3Si)_2O$]				

The base (I) (1·82 g.) was boiled with 95% ethanol–water (2 ml.) for 48 hr., and excess of water was then added. The solution was saturated with sodium chloride, and the upper insoluble layer was washed with water, to give hexamethyldisiloxane (0·73 g., 82%), n_D^{24} 1·3768.

Treatment of the organosilicon bases with 90% ethanol–water containing 5% of potassium hydroxide at room temperature (*ca.* 18°) gave the following results :

Compound (I)		Compound (II)		Compound (III)	
Time, hr.	n_D^{23}	Time, hr.	n_D^{22}	Time, hr.	n_D^{22}
0	(1·5000) [(I)]	0	1·4874 [(II)]	0	1·4964 [(III)]
¼	1·3770 [$(Me_3Si)_2O$]	¼	1·4676	¼	1·4928
		2½	1·4080	2½	1·4880
		8	1·3778 [$(Me_3Si)_2O$]		

When the base (I) (0·82 g.) was added to the aqueous-alcoholic alkali (2 ml.) considerable heat was evolved. After ¼ hr. excess of saturated aqueous sodium chloride solution was added and the upper layer of liquid was separated and washed with water to give hexamethyldisiloxane (0·39 g., 96%), n_D^{23} 1·3760. The base (II), similarly treated for 8 hr., gave hexamethyldisiloxane in 81% yield.

The base (III) (0·62 g.), treated with the boiling aqueous alcoholic alkali (2 ml.) for 1 hr., gave hexamethyldisiloxane (0·38 g., 91%).

Acidic cleavage. The 4-derivative (I) (0·435 g.) gave a clear solution in 2N-aqueous hydrochloric acid (2·5 ml.) which quickly became cloudy, and an upper insoluble layer was formed. After ½ hr. this layer was separated, washed with water, and identified as hexamethyldisiloxane (0·20 g., 94%), b. p. 101°, n_D^{23} 1·3762.

The solution of the 2-derivative (II) in the same solvent remained clear for a longer period and hexaethyldisiloxane was obtained in 86% yield after 1½ hr. The solution of the disubstituted picoline (III) remained clear for much longer, but hexamethyldisiloxane was obtained in 92% yield after 16 hr.

Ultraviolet absorption spectra. These (see Table) were determined with a Unicam S.P. 500 Spectrophotometer, *n*-hexane being used as solvent. The maxima in the 220-mμ region probably corresponds with the maximum which is just below 200 mμ for pyridine (Pickett, Corning, Wieder, Semenov, and Buckley, *J. Amer. Chem. Soc.*, 1953, **75**, **1618**). The most intense maxima in the 260 mμ region for α- and γ-picoline in *cyclo*hexane are at 262 (ε 2740) and 256 mμ (ε 1630), respectively (Herington, *loc. cit.*).

Base	$\lambda_{max.}$(mμ) (ε in parentheses)			
4-(Trimethylsilylmethyl)pyridine	216·5 (8020)	252 (1320)	257 (1350)	—
2-(Trimethylsilylmethyl)pyridine	216 (7600)	264 (2920)	269 (3040)	276·5 * (2090)
2-[Bis(trimethylsilyl)methyl]pyridine ...	222 (11,700)	268·5 * (3350)	273·5 (3600)	280·5 * (2450)

* Inflexion.

We thank the Director of the Chemical Research Laboratory, Teddington, for use of a spinning-band fractionating column.

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Quinoxalines and Related Compounds. Part II. The Preparation of* NN'*-Dimethyl-*o*-phenylenediamine and* N*-Methyl-*o*-phenylenediamine.*

By G. W. H. CHEESEMAN.

[Reprint Order No. 6395.]

THE following three-stage synthesis of *NN'*-dimethyl-*o*-phenylenediamine has been described by Elderfield and Meyer (*J. Amer. Chem. Soc.*, 1954, **76**, 1887). *o*-Phenylenediamine was converted into *NN'*-ditoluene-*p*-sulphonyl-*o*-phenylenediamine which on treatment with methyl sulphate and alkali gave the *NN'*-dimethyl-diamide; hydrolysis with glacial acetic acid and concentrated sulphuric acid then furnished the *NN'*-dimethyl-diamine in *ca.* 6% overall yield. It has now been found that the diamine can be obtained in excellent yield by the hydrolysis of the intermediate dimethyl compound with aqueous sulphuric acid. With this modification and Stetter's method (*Chem. Ber.*, 1953, **86**, 161) for the preparation of *NN'*-ditoluene-*p*-sulphonyl-*o*-phenylenediamine, *NN'*-dimethyl-*o*-phenylenediamine was obtained in 70% overall yield.

NNN'-Tritoluene-*p*-sulphonyl-*o*-phenylenediamine was obtained from the interaction of three mols. of toluene-*p*-sulphonyl chloride and one of *o*-phenylenediamine, or equimolar amounts of the chloride and *NN'*-ditoluene-*p*-sulphonyl-*o*-phenylenediamine. This derivative was converted into *NN'*-ditoluene-*p*-sulphonyl-*o*-phenylenediamine and *NN'*-dimethyl-*NN'*-ditoluene-*p*-sulphonyl-*o*-phenylenediamine by treatment with methyl sulphate and aqueous-methanolic sodium hydroxide. Methylation with methyl iodide and methanolic sodium methoxide yielded *N*-methyl-*NNN'*-tritoluene-*p*-sulphonyl-*o*-phenylenediamine which on hydrolysis with aqueous sulphuric acid gave *N*-methyl-*o*-phenylenediamine in high yield. Poorer yields of diamine were obtained from hydrolyses with concentrated sulphuric acid–acetic acid; acetylation and subsequent ring closure

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* Part I, *J.*, 1955, 1804.

occurred and thus 1 : 2-dimethylbenziminazole was formed. The hydrolysis, by aqueous sulphuric acid, of *N*-methyl-*NN'*-ditoluene-*p*-sulphonyl-*o*-phenylenediamine, prepared from *NN'*-ditoluene-*p*-sulphonyl-*o*-phenylenediamine by Stetter's method (*loc. cit.*), also furnished *N*-methyl-*o*-phenylenediamine in high yield.

N-Methyl-*o*-phenylenediamine has been prepared from *o*-nitroaniline by a four-stage synthesis (Usherwood and Whiteley, *J.*, 1923, 1084; Phillips, *J.*, 1929, 2820; Cheeseman, *J.*, 1955, 1804). An alternative synthesis, based on *o*-chloronitrobenzene, involves two reactions under pressure (Elderfield and Meyer, *J. Amer. Chem. Soc.*, 1954, **76**, 1891). The three-stage preparation of the diamine now available from *o*-phenylenediamine *via NNN'*-tritoluene-*p*-sulphonyl-*o*-phenylenediamine and its *N*-methyl derivative was carried out in 43% overall yield and that *via NN'*-ditoluene-*p*-sulphonyl-*o*-phenylenediamine and its *N*-methyl derivative in 63% overall yield.

Experimental.—Pyridine was dried over potassium hydroxide and distilled.

NN'-*Ditoluene*-p-*sulphonyl*-o-*phenylenediamine.* This was prepared by Stetter's method (*loc. cit.*). The crude product was washed with water and heated under reflux with 96% ethanol (1 l.). After cooling, the diamide (153 g., 92%), m. p. 204—205°, was collected. Stetter gives m. p. 203° (corr.).

NN'-*Dimethyl*-NN'-*ditoluene*-p-*sulphonyl*-o-*phenylenediamine.* The above diamide (20·8 g., 0·05 mole) was boiled with 4N-sodium hydroxide (25 c.c., 0·1 mole). Methyl sulphate (9 c.c., 0·1 mole) was added to the cooled suspension and, after the initial reaction had moderated, the mixture was gently boiled for 5 min. After cooling, suspended solid was crushed and 4N-sodium hydroxide (25 c.c.) and methyl sulphate (9 c.c.) were added. The mixture was again boiled for 5 min. After two further similar treatments, the solid was filtered from the hot mixture and boiled with 0·75N-sodium hydroxide (400 c.c.). The alkali-insoluble material crystallised from 96% ethanol (375 c.c.) as colourless needles (19·7 g., 89%), m. p. 177—178°. Stetter (*loc. cit.*) gives m. p. 175° (corr.); Elderfield and Meyer (*J. Amer. Chem. Soc.*, 1954, **76**, 1887) give m. p. 178—179°.

NN'-*Dimethyl*-o-*phenylenediamine.* The dimethyl-diamide (22·2 g., 0·05 mole) was heated in concentrated sulphuric acid (20 c.c.) and water (2 c.c.) on the steam-bath for 4 hr., then poured into ice-water. 10N-Sodium hydroxide (100 c.c.) was added and the mixture diluted to *ca.* 1 l. to prevent the separation of sodium sulphate. Extraction with ether and evaporation of the dried (Na_2SO_4) extracts gave a dark oil which on distillation yielded *NN'*-dimethyl-*o*-phenylenediamine (5·85 g., 86%), b. p. 93°/1·7 mm., $n_D^{17\cdot5}$ 1·5955. This diamine readily crystallised as colourless needles, m. p. 31·5°; it discoloured on exposure to air. Elderfield and Meyer (*loc. cit.*) give b. p. 108·5—109°/5 mm., m. p. 30·5—31°, $n_D^{25\cdot5}$ 1·5914. The non-volatile fraction solidified and after two crystallisations from ethanol (charcoal) gave colourless needles of NN'-*dimethyl*-N-*toluene*-p-*sulphonyl*-o-*phenylenediamine*, m. p. 134—135° (Found: C, 62·4; H, 6·3; N, 9·8; S, 10·8. $C_{15}H_{18}O_2N_2S$ requires C, 62·05; H, 6·25; N, 9·65; S, 11·0%).

NNN'-*Tritoluene*-p-*sulphonyl*-o-*phenylenediamine.* (*a*) Toluene-*p*-sulphonyl chloride (172 g., 0·9 mole), *o*-phenylenediamine (32·4 g., 0·3 mole), and pyridine (150 c.c.) were heated on the steam-bath for 6½ hr. and then poured into excess of 2N-hydrochloric acid. The crude product gradually solidified and was filtered off, washed with water, and dried. Crystallisation from ethanol (4 l.) gave NNN'-*tritoluene*-p-*sulphonyl*-o-*phenylenediamine* (116 g., 68%) as needles, m. p. (mainly) 156—157°. The analytical sample, recrystallised from ethanol (30 parts), had m. p. 156—157° (Found: C, 56·8; H, 4·2; N, 5·1; S, 17·0. $C_{27}H_{26}O_6N_2S_3$ requires C, 56·8; H, 4·6; N, 4·9; S, 16·9%).

(*b*) Toluene-*p*-sulphonyl chloride (19·1 g., 0·1 mole), *NN'*-ditoluene-*p*-sulphonyl-*o*-phenylenediamine (41·6 g., 0·1 mole) and pyridine (50 c.c.) were heated on the steam-bath for 6½ hr. Colourless needles of *NNN'*-tritoluene-*p*-sulphonyl-*o*-phenylenediamine (39 g., 68%), m. p. and mixed m. p. 156—157°, were isolated as described under (*a*) above.

N-*Methyl*-NNN'-*tritoluene*-p-*sulphonyl*-o-*phenylenediamine.* The above tritoluene-*p*-sulphonyl compound (131·3 g., 0·23 mole), dissolved in sodium methoxide solution (1 equiv.), from sodium (5·29 g.) and dry methanol (1 l.), and methyl iodide (120 g.) were heated under reflux for 24 hr. The mixture was cooled and made alkaline with methanolic sodium methoxide (1 equiv.), and the crystalline precipitate of N-*methyl*-NNN'-*tritoluene*-p-*sulphonyl*-o-*phenylenediamine* (105 g., 78%), m. p. 200—202°, collected. Crystallisation from methanol (300 parts) gave colourless prisms, m. p. 202—203° (Found: C, 57·0; H, 4·85; N, 4·65; S, 16·1. $C_{28}H_{28}O_6N_2S_3$ requires C, 57·5; H, 4·8; N, 4·8; S, 16·45%). Acidification of the initial alkaline filtrate with glacial acetic acid precipitated unchanged starting material (23 g., recovery 17·5%), m. p. (mainly) 156—157°.

N-*Methyl*-o-*phenylenediamine*. (*a*) The preceding methyl derivative (29·3 g., 0·05 mole) was dissolved in concentrated sulphuric acid (30 c.c.) and water (3 c.c.). The solution was heated on the steam-bath for 3½ hr. and the product isolated similarly to *NN'*-dimethyl-*o*-phenylenediamine above. Distillation gave *N*-methyl-*o*-phenylenediamine (5·0 g., 82%), b. p. 92—93°/1·7 mm., m. p. 22°, n_D^{17} 1·615; it discoloured on exposure to air. Elderfield and Meyer (*J. Amer. Chem. Soc.*, 1954, **76**, 1891) give b. p. 123—124°/10 mm., m. p.s 7·5—7·9° and 21—23°, $n_D^{25.8}$ 1·6111. The diamine dihydrochloride was converted into 1 : 2-dihydro-1 : 3-dimethyl-2-oxoquinoxaline, m. p. and mixed m. p. 85·5—86·5°, by Kehrmann and Messinger's method (*Ber.*, 1892, **25**, 1629), and into 1 : 2-dimethylbenziminazole, m. p. and mixed m. p. 110·5—111·5°, by Phillips's method (*loc. cit.*) (Found : C, 74·3; H, 6·75. Calc. for $C_9H_{10}N_2$: C, 73·9; H, 6·9%).

(*b*) Hydrolysis of *N*-methyl-*NN'*-ditoluene-*p*-sulphonyl-*o*-phenylenediamine (21·5 g., 0·05 mole; Stetter, *loc. cit.*) with concentrated sulphuric acid (20 c.c.) and water (2 c.c.) for 4 hr. on the steam-bath similarly gave the diamine, b. p. 96—97·5/1·5 mm., m. p. 22°, $n_D^{18.5}$ 1·6133, in 82% yield.

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