NOTES.

651. *A New Double Spoon Gauge.*

By J. D. SWANWICK.

SINCE the introduction [1] in 1906 of the first glass Bourdon gauge, there have been many developments of spoon, spiral, and diaphragm gauges,[2] in general suitable only for measurement of pressures above 10^{-1} mm. Hg.

Studies on the vapour pressures of the alkoxides [3] required a Pyrex-glass gauge capable of detecting pressure differences down to 10^{-2} mm. Hg and sufficiently robust to withstand cleaning with liquid reagents. If the sensitivity of a gauge is defined as the ratio of the deflection of the pointer to the applied pressure difference across the gauge, it was the author's experience that a sensitivity of about 3 mm. per mm. Hg was the optimum for a single spoon gauge with a mechanical pointer. Less sensitive gauges did not allow accurate pressure measurements, and more sensitive gauges were difficult to make and more easily broken both by normal manipulation and by small pressure differences to which such a gauge was temporarily subjected during actual pressure measurements. Spiral gauges are more robust than spoon gauges but are very difficult to clean.

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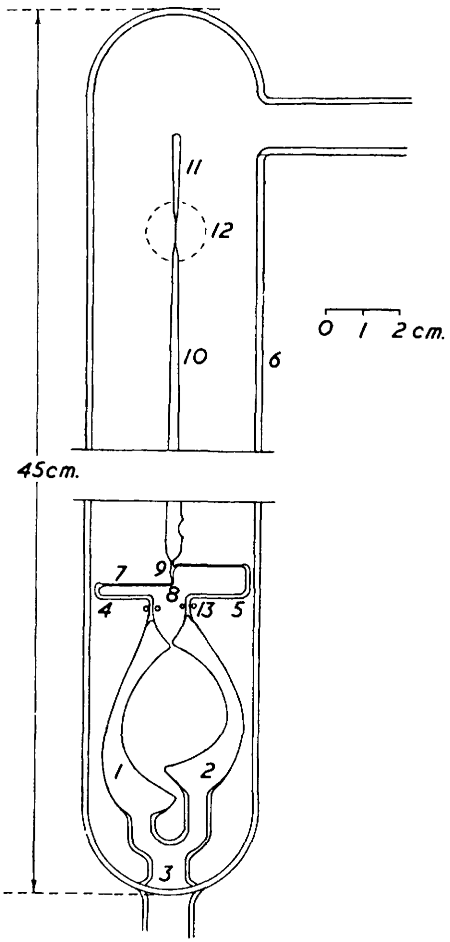
[1] Ladenburg, *Verhandl. deutsch. phys. Ges.*, 1906, **8**, 20.
[2] Cf. Swanwick, Ph.D. Thesis, London, 1956.
[3] Bradley and Swanwick, preceding paper.

The new double spoon gauge now reported (see Figure) has a sensitivity 8—10 times that of the single spoon gauges used in its construction; the lever principle is adapted to the relative movement of two opposed spoon gauges, by causing the fulcrum of the lever-type pointer to move in the opposite direction to the applied force.



The two spoon gauges 1 and 2 communicate with each other and with the vaporisation chamber through the tube 3. Rigid glass supports 4 and 5 of diameter 1 mm. are sealed to the gauges, extending in the line of movement of the gauges to within about 1 mm. of the wall of the jacket 6. The support 4 carries a glass fibre 7 which is sealed to the lower extremity 8 of the pointer, and support 5 is likewise connected to the fulcrum 9. A thickness of 0·13 mm. for the fibres gave a suitable compromise between flexibility and strength. The pointer 10 (length 25 cm.) had to be made of minimum weight consistent with rigidity, and the optimum value was found to be *ca.* 20 mg. A fixed pointer was sealed to the upper end of the jacket, and the extremities of both pointers were drawn out to short fibres, the thickness of which was arranged to appear similar to the thickness of the scale divisions on the objective of the telescope 12 through which they were viewed. The optimum distance of the fulcrum from the lower end of the pointer was found to be about 5 mm., the gauge losing sensitivity as this distance was increased and a shorter distance resulting both in failure of the suspension system to support the pointer in a vertical position and in loss of sensitivity due to the finite rigidity of the horizontal connecting fibres.

Gauges with a sensitivity between 5 and 8 mm. per mm. Hg were satisfactory for a pressure difference of 10^{-2} mm.

A drawback of a spoon gauge is its inability to withstand large pressure differences, although this has been partially overcome in the double spoon gauge by the incorporation of four parallel horizontal bars 1 mm. in diameter, shown in end section (13) in the Figure, and placed so that the traverse of the spoon gauges was limited to less than 0·5 mm. Gauges capable of withstanding a pressure difference as great as one atmosphere have not been constructed but it is evident that stronger gauges will be considerably easier to assemble.

Two rigid glass supports (diam. 2—3 mm.) were sealed on to the tube 3 at their lower end and terminated at their upper end in a ring about 10 mm. in diameter held ~10 mm. below the upper extremity of the pointer. This ring and its supports (not shown in the Figure) were not essential to the working of the gauge but were helpful in the delicate process of inserting and sealing the gauge assembly into the glass jacket.

The double spoon gauge was very stable when subjected to vibration and was superior in this respect to single spoon gauges of similar sensitivity. This property is due to the opposing glass fibres which also absorb sudden shocks which would fracture a conventional gauge.

Birkbeck College, Malet St., London, W.C.1.

[*Received, March* 24*th*, 1958.]

652. *Vinylanthracenes, and the Polymerization of the 9-Isomer.*

By Ernst D. Bergmann and Dov Katz.

The use of fluorescent substances embedded in a non-fluorescent polymer for scintillation counters led us to seek a method of preparing polymers which contained fluorescent radicals in their *molecule.* Studying the vinylanthracenes (1-, 2-, and 9-), their polymers, and co-polymers we have, in principle, achieved our aim. Vinylanthracenes have also been prepared by Hawkins.[1] The constants and spectra of our compounds are summarized in the Table. The addition of a conjugated ethylenic bond in the 2- or 9-position of anthracene changes the fluorescence from blue to yellow, but 1-vinylanthracene retains the blue fluorescence of anthracene. The hydroxyl frequency in 1-1′-anthrylethanol is lower than that of the 2′- and 9′-isomers; this may be due to the hydroxyl group's entering the field of the π-electrons of the middle ring. A similar phenomenon was observed by Anet and Bavin [2] for 9-(hydroxyalkyl)fluorenes.

	R.S.*	M. p.	Found (%)		Required (%)		Colour †	Fluor.‡
			C	H	C	H		
Oximes ($C_{16}H_{13}NO$) § of								
9-acetylanthracene	E	185—186°	81·9	5·7	81·7	5·6	Y	Y
1-acetylanthracene	E	162—163	81·6	6·0	81·7	5·6	YB	LB
2-acetylanthracene	E	247—248	82·1	5·4	81·7	5·6	Y	LB
1-x′-*Anthrylethanols* ($C_{16}H_{14}O$) ‖								
$x = 9$	E,B	121—122	86·8	6·3	86·5	6·3	C	DB
$x = 1$	E	114—115	86·3	6·5	86·5	6·3	PY	LB
$x = 2$	E	156—157	86·5	6·4	86·5	6·3	PY	GB
Acetates ($C_{18}H_{16}O_2$) of								
1-9′-anthrylethanol	E	99—100	82·1	6·4	81·8	6·1	C	DB
1-2′-anthrylethanol	M	126—127	82·3	6·1	81·8	6·1	C	B
Benzoates ($C_{23}H_{18}O_2$) of								
1-9′-anthrylethanol	E	88—89	84·2	5·7	84·6	5·6	C	DB
1-2′-anthrylethanol	E	157—158	84·0	5·6	84·6	5·6	C	B
Vinylanthracenes ($C_{16}H_{12}$) ‖								
9-	M	64—65	93·8	5·8	94·1	5·9	Y	LY
1-	E	62—63	94·2	5·9	94·1	5·9	Y	LB
2-	E	186—187	93·5	6·2	94·1	5·9	Y	GY

Spectra: Ultraviolet (in ethanol) [mμ (log ε)]; infrared (KBr discs); fluorescence (in ethanol).

1-Vinylanthracene ...	255 (5·15), 369 (3·86), 390 (3·76). ν(C=CH$_2$) 990, 910 cm.$^{-1}$. Fluor. 410 mμ (m), 427 mμ (s), 455 mμ (m).
2-Vinylanthracene ...	220 (4·26), 258 (4·79), 266 (4·93), 277 (5·04), 314 (3·32), 328 (3·54), 345 (3·75), 362 (3·86), 383 (3·72). ν(C=CH$_2$) 990, 910 cm.$^{-1}$. Fluor. 408 mμ (m), 426 mμ (m).
9-Vinylanthracene ...	218 (4·00), 223 (4·00), 256 (5·25), 350 (3·70), 368 (3·85), 388 (3·78). ν(C=CH$_2$) 990, 933 cm.$^{-1}$. Fluor. 430 mμ (s).
1-1′-Anthrylethanol...	254 (5·08), 327 (3·42), 344 (3·20), 362 (3·87), 381 (3·81). ν(C–OH) 3226 cm.$^{-1}$. Fluor. 384 mμ (w), 408 mμ (s), 433 mμ (w).
1-2′-Anthrylethanol ¶	256 (5·26), 325 (3·45), 340 (3·67), 357 (3·79), 376 (3·70). ν(C–OH) 3249 cm.$^{-1}$. Fluor. 409 mμ (m).
1-9′-Anthrylethanol...	256 (5·18), 327 (3·11), 332 (3·45), 348 (3·74), 366 (3·90), 386 (3·90). ν(C–OH) 3247 cm.$^{-1}$. Fluor. 393 mμ (w), 412 mμ (s), 437 mμ (w).

* Recrystallizing solvent: E, ethanol; B, benzene; M, methanol.

† Y, yellow; YB, yellow-brown; PY, pale yellow; C, colourless.

‡ Y, yellow; B, blue; L, light; D, dark; GB, greenish blue; GY, greenish yellow (fluorescence excited at 2537 Å).

§ Described by Martynoff,[3] after submission of this paper.

‖ Described by Hawkins.[1]

¶ The infrared spectra of 1-2′-anthrylethanol and its acetate show an indication of the presence of 2-vinylanthracene; this may be due to the pressure applied in the preparation of the potassium bromide pellet causing some dehydration.

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[1] Hawkins, *J.*, 1957, 3858.

[2] Anet and Bavin, *Canad. J. Chem.*, 1956, **34**, 1756; Goldman and Crisler, *J. Org. Chem.*, 1958, **23**, 751.

[3] Martynoff, *Bull. Soc. chim. France*, 1958, 164.

The polymerizations were concerned mainly with 9-vinylanthracene. Radical polymerization (induced by benzoyl peroxide) is very slow, but copolymerization with styrene is quicker, the anthracene derivative inhibiting the polymerization of styrene. As the copolymer shows the typical blue fluorescence of anthracene we assume that its carbon backbone carries $C_{14}H_9$ (and C_6H_5) side groups.

The quantity of the anthracene derivative in the copolymer can be determined by comparison of the intensities of the ultraviolet absorptions at 262 mμ for the copolymer, anthracene, and polystyrene. Thus, when the original mixture contained 25% (w/w) of 9-vinylanthracene, the copolymer contained 4·5% of it.

The cationic polymerization of 9-vinylanthracene with stannic chloride as catalyst is very fast. If small quantities of catalyst are used, one obtains a soluble polymer of pure blue fluorescence, and with larger amounts of the catalyst insoluble products of slight yellow fluorescence are obtained. It can be assumed that the former is a pure vinyl polymer and the latter contains cross-links which involve the anthracene nuclei. In no case have the vinyl bands (at 990 and 933 $cm.^{-1}$) been detected in the infrared spectrum of the polymers, and their ultraviolet spectrum is identical with that of anthracene.

Experimental.—1- *and* 2-*Acetylanthracene.* Gore's method [4] was used; generally the ratio of anthracene : acetyl chloride : aluminium chloride was 1 : 3 : 3 and benzene was used as diluent (300 ml. for 45 g. of anthracene). The aluminium chloride was added, with stirring, at −3°, and the reaction continued for 1 hr. at about 5° and for 25 hr. at room temperature. After decomposition with ice and concentrated hydrochloric acid (1 : 1) the product was treated *in vacuo* to remove acetophenone and dissolved in boiling benzene. Upon cooling, 2-acetylanthracene crystallized; the 1-isomer was isolated by evaporation of the mother liquor and recrystallization of the residue from light petroleum (b. p. 60—90°) (total yield, 41%; ratio of 2 : 1-acetylanthracene, 1 : 4).

The three acetylanthracenes were reduced with lithium aluminium hydride in ether (1- and 9-compound) or tetrahydrofuran (2-compound) (yield, 80, 95, and 100% respectively).

Vinylanthracenes.—The 1-*x*-anthrylethanol (5 g.) was heated with potassium hydrogen sulphate (0·25—0·5 g.) and copper powder (0·05—0·1 g.) at 1 mm. pressure. The products distilled at 160—170°. 9-Vinylanthracene (yield, 85—90%) was recrystallized from methanol, the other two isomers (yields, 60—65 and 65—70%) from ethanol. The addition of copper powder to the dehydration mixture reduced the tendency to polymerization.

Polymerizations.—9-Vinylanthracene (0·4 g.) and benzoyl peroxide (0·016 g.) were sealed in glass tubes at 1 mm. pressure and heated at 90° for 48 hr. and then at 110° for 20 days. (The polymerization was, therefore, initially catalyzed, but in the later stages thermal.) After this time, the product was solid at 110°. It was dissolved in benzene and the yellowish polymer precipitated with methanol (softening point, 220—230°).

9-Vinylanthracene and styrene were copolymerized by the same technique (with 2% of benzoyl peroxide). The reaction is catalytic only in its first stages. The mixture was heated for 48 hr. at 90° and then at 110° until, upon cooling, the mass broke up or separated from the walls, owing to the reduction in molar volume of the polymer. When the amount of vinyl anthracene in the mixture was raised from 0 to 1, 5, 10, and 25% (by weight), the polymerization time increased from 2 hr. to 48, 72, 72, hr., and 107 days, respectively, and the conversion decreased from 97 to 97, 92, 83, and 61%, respectively.

For cationic polymerizations, 9-vinylanthracene (0·75 g.) was mixed with 0·75 g. of anhydrous benzene, and an aliquot part of a 38% solution of stannic chloride in benzene was added at 20°. When the concentration of the chloride in the mixture was 0·15% and 0·25%, viscous, yellow solutions were obtained, the conversions being 14 and 40%, respectively. Also, with 0·5% of stannic chloride, a very viscous solution was obtained. At higher concentrations of the catalyst (1·0 and 2·5%), the polymer was a dark-brown insoluble solid, which was precipitated after 10 and 2 min., respectively. The first soluble polymer shows a pure blue fluorescence (437 mμ in chloroform), and a spectrum practically identical with that of anthracene.

SCIENTIFIC DEPARTMENT, ISRAEL MINISTRY OF DEFENCE.

[*Received, January 23rd*, 1958.]

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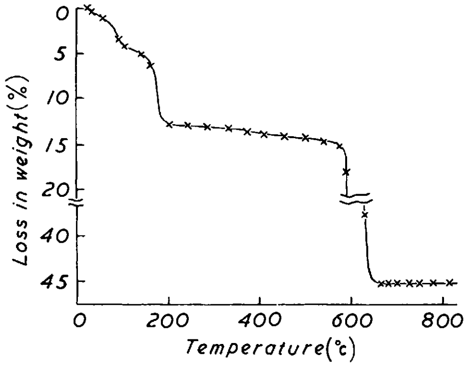
[4] Gore, *J. Org. Chem.*, 1957, **22**, 135.

653. *The Preparation and Properties of Some Plutonium Compounds. Part VIII.*[*] *Plutonium*(IV) *Sulphate.*

By J. L. Drummond and G. A. Welch.

Cunningham,[1] and Harvey, Heal, Maddock, and Rowley,[2] reported that anhydrous plutonium(IV) sulphate was obtained by evaporating dilute sulphuric acid solutions of quadrivalent plutonium salts, followed by gentle ignition to remove the excess of acid; also that it was stable in air and could readily be weighed as such. It was soluble in dilute mineral acids, but deposited crystals of the tetrahydrate from concentrated solutions in sulphuric acid. Anderson[3] precipitated the same hydrate by adding methanol to the solution, and found that if the hydrate was dried in air at 153° then $\mathrm{Pu(SO_4)_2,\frac{1}{3}H_2O}$ was formed. Further heating at 280° decomposed it to a basic sulphate and ignition at 800° entirely to the dioxide. Allison[4] found that the anhydrous salt has a Pu : $\mathrm{SO_4}$ weight ratio of 1·26 compared with the theoretical value of 1·24, but recommended it as a gravimetric standard.

Thermogravimetric curve of plutonium(IV) *sulphate.*



While seeking a suitable gravimetric standard for plutonium, we studied the preparation, composition, and stability of the quadrivalent sulphate. The anhydrous salt was prepared from specially purified plutonium nitrate solutions by repeated evaporation and fuming with sulphuric acid. The sulphate was heated in an open container at a fixed temperature between 450° and 650°, the thermal stability range quoted by Dawson and Elliott[5] from thermogravimetric data. The product was hygroscopic, and even when cooled in dry air and weighed in a closed weighing bottle it was not possible to attain constant weight. There was a steady loss of 0·1—0·2% per 15 minutes' heating at any temperature, or a more pronounced loss if the temperature was raised. Therefore, samples were weighed after being heated at the desired temperature for 15 min. only. The plutonium content was determined by ignition to 870° to form the oxide[6] $\mathrm{PuO_{2\cdot09}}$, and the weight ratio of plutonium sulphate : plutonium oxide was calculated. The mean ratios obtained, with their spread, from the number of determinations shown in parentheses at given temperatures, were: 450° (2), 1·600 ± 0·003; 480° (5), 1·592 ± 0·002; 490° (4), 1·588 ± 0·004; 510° (2), 1·584 ± 0·001; 520° (8), 1·583 ± 0·005; 570° (2), 1·569 ± 0·002. They thus vary with the temperature of preparation of the sulphate on both sides of the theoretical ratio of 1·582. The variation was confirmed by careful examination of the compound on a sensitive thermobalance; the heat-stability curve of plutonium sulphate containing a little free acid is in the Figure. Thus the anhydrous sulphate is not a suitable weighing form for plutonium gravimetry.

In some preparations, the plutonium sulphate contained yellow patches which were converted into the normal pink form by repeated fuming to dryness with sulphuric acid. The yellow material was believed to be plutonyl sulphate, as it was soluble in water and

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[*] Part VII, *J.*, 1957, 4785.

[1] Cunningham, "The Actinide Elements," McGraw-Hill Book Co. Inc., New York, 1954, p. 408.

[2] Harvey, Heal, Maddock, and Rowley, *J.*, 1947, 1010.

[3] Anderson, "The Transuranic Elements," McGraw-Hill Book Co. Inc., New York, 1949, p. 796.

[4] Allison, Report P.D.B.-60 (Atomic Energy of Canada Ltd.).

[5] Dawson and Elliott, A.E.R.E. C/R. 1207 (U.K. Atomic Energy Authority).

[6] Drummond and Welch, *J.*, 1957, 4781.

was not formed if plutonium(VI) was absent originally. However, the maximum yield of this material was about 10%, even from pure plutonyl nitrate.

Anhydrous plutonium(IV) sulphate was soluble in 5N-mineral acids, although crystals of a less soluble hydrate were sometimes deposited on standing. It also dissolved in water. An approximately 0·5M-aqueous plutonium sulphate solution was stable, but a 0·05M-solution became cloudy after 1 hr. More dilute solutions rapidly became turbid and the plutonium which was not precipitated was probably colloidal. Thus the stability of a solution of plutonium sulphate in water, and to some extent in dilute sulphuric acid, depends upon the concentration of the salt, probably owing to formation of an anionic complex by the sulphate ions liberated by partial hydrolysis, thus preventing complete hydrolysis. A stable solution of plutonium sulphate in water was shown to contain much anionic and negligible cationic plutonium by electromigration.

Experimental.—*Anhydrous plutonium*(IV) *sulphate.* Pure plutonium nitrate solutions (0·2—0·5 g. of Pu), mixed with sulphuric acid (0·5—1 ml. of 18N) and a little sulphur dioxide water to reduce any plutonium(VI), were evaporated to dryness in small tared silica weighing bottles and heated at fixed temperatures between 450° and 570° for 15 min. The bottles were covered and cooled in dry air and weighed on a semimicro balance. The plutonium sulphate was then moistened with 18N-sulphuric acid and heated at the same temperature until the weight was constant to within 0·1%.

The silica spiral thermobalance has been described.[7]

Acknowledgment is made to Heather M. Ockenden for the thermogravimetry, and to Sir Leonard Owen, the Managing Director of the Industrial Group of this Authority, for permission to publish this note.

U.K. ATOMIC ENERGY AUTHORITY, DOUNREAY EXPERIMENTAL REACTOR ESTABLISHMENT,
DOUNREAY, nr. THURSO, CAITHNESS.
[*Received, March 7th,* 1958.]

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[7] Brown, Ockenden, and Welch, *J.*, 1955, 3932.

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654. *Solvated Triphenylmethane Derivatives containing Bromine.*

By J. E. DRIVER and (MISS) T. F. LAI.

TRIPHENYLMETHANE derivatives which form molecular compounds with hydrocarbon and chlorohydrocarbon solvents were described by Driver and Mok.[1] Mr. H. M. Powell suggested that solvated compounds of this type containing bromine might be particularly suitable for crystallographic study, and the examples tabulated have therefore been prepared.

Compound (*A*)				
Br	OH	Me	Solvent (*B*)	*A* : *B* (mols.)
3	4′ : 4″	—	Benzene	1 : 1
			Toluene	1 : 1
3	4′ : 4″	3′ : 3″	*p*-Xylene	1 : 1
3	4′ : 4″	2′ : 2″	Benzene	1 : 1
			p-Xylene	1 : 1
			Chlorobenzene	1 : 1
			Bromobenzene	1 : 1
3	2′ : 2″	5′ : 5″	*p*-Xylene	2 : 1
3	4′ : 4″	3′ : 3″ : 5′ : 5″	Benzene	1 : 1
4	4′ : 4″	—	Benzene	2 : 3
4	4′ : 4″	3′ : 3″ : 5′ : 5″	Benzene	3 : 2
2	4′ : 4″	—	Benzene	*ca.* 1 : 1

Experimental.—Phenols, bromobenzaldehydes, hydrocarbons, and halogenohydrocarbons were suitably purified, and distilled within 1° or had sharp m. p.s. Microanalyses are by Dr. Zimmermann, Melbourne.

3-*Bromo*-4′ : 4″-*dihydroxytriphenylmethane.* A solution of *m*-bromobenzaldehyde (9·2 g.) and phenol (10·4 g.) in acetic acid (10 ml.) was cooled to 0°, and sulphuric acid (3 ml.) in acetic acid (10 ml.) was added dropwise with stirring. The mixture was kept at *ca.* 0° for 16 hr. and then stirred into crushed ice. The orange solid (17 g.) crystallized as the *benzene compound*

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[1] Driver and Mok, *J.*, 1955, 3914.

in pale yellow needles which melted at 156—157° with loss of solvent (Found: loss at 132°/3 mm., 17·3. $C_{19}H_{15}O_2Br,C_6H_6$ requires C_6H_6, 18·0%). The *toluene compound* softened at 110—120° with loss of solvent (Found: loss at 132°/3 mm., 20·8. $C_{19}H_{15}O_2Br,C_7H_8$ requires C_7H_8, 20·6%). The unsolvated *compound* separated from chlorobenzene or bromobenzene in stout, yellow prisms, m. p. 159—160°, though under some conditions solvated crystals were formed from these solvents (Found: C, 64·3; H, 4·4; Br, 22·4%; *M*, 362. $C_{19}H_{15}O_2Br$ requires C, 64·2; H, 4·2; Br, 22·5%; *M*, 355). The *dibenzoyl derivative* separated from light petroleum in needles, m. p. 164—165° (Found: C, 70·6; H, 4·4; Br, 13·9%; *M*, 618. $C_{33}H_{23}O_4Br$ requires C, 70·3; H, 4·1; Br, 14·2%; *M*, 563).

3-*Bromo*-4′ : 4″-*dihydroxy*-3′ : 3″-*dimethyltriphenylmethane* was prepared from *m*-bromobenzaldehyde (9·2 g.) and *o*-cresol (11·9 g.) (7 days). The product (15 g.) yielded the p-*xylene compound* by slow crystallization as large, pale yellow plates which melted at 60—65° with loss of solvent (Found: loss at 132°/3 mm., 21·0. $C_{21}H_{19}O_2Br,C_8H_{10}$ requires C_8H_{10}, 21·7. Found, for the unsolvated compound: C, 65·9; H, 5·4; Br, 19·9%; *M*, 352. $C_{21}H_{19}O_2Br$ requires C, 65·8; H, 5·0; Br, 20·9%; *M*, 383).

3-*Bromo*-4′ : 4″-*dihydroxy*-2′ : 2″-*dimethyltriphenylmethane* was prepared from *m*-bromobenzaldehyde (4·5 g.) and *m*-cresol (6 g.) (18 hr.). The product (7·5 g.) yielded the *benzene compound* in needles, m. p. 216—218° (decomp.) (Found: loss at 100°/3 mm., 17·0. $C_{21}H_{19}O_2Br,C_6H_6$ requires C_6H_6, 16·9%). The unsolvated compound, made by heating the benzene compound at 100°/3 mm., melted at 220—221° (decomp.) (Found: C, 66·0; H, 5·1; Br, 20·4%; *M*, 400). The p-*xylene compound* formed pale yellow crystals, m. p. 218° (decomp.) (Found: loss at 132°/3 mm., 20·9%). The *chlorobenzene compound* formed yellow crystals, m. p. 210—212° (decomp.) (Found: loss at 132°/3 mm., 22·6. $C_{21}H_{19}O_2Br,C_6H_5Cl$ requires C_6H_5Cl, 22·7%). The *bromobenzene compound* melted at 215—216° (decomp) (Found: loss at 155°/3 mm., 28·6. $C_{21}H_{19}O_2Br,C_6H_5Br$ requires C_6H_5Br, 29·1%).

3-*Bromo*-2′ : 2″-*dihydroxy*-5′ : 5″-*dimethyltriphenylmethane* was prepared from *m*-bromobenzaldehyde (4·5 g.) and *p*-cresol (6 g.) (18 hr.). The crude product (7·5 g.) was extracted with sodium hydroxide solution. Acidification with hydrochloric acid gave a brown resin, which yielded the p-*xylene compound* in colourless plates, m. p. 140—144° with loss of solvent (Found: loss at 132°/3 mm., 12·0. $2C_{21}H_{19}O_2Br,C_8H_{10}$ requires C_8H_{10}, 12·2%). The unsolvated compound, prepared by heating the *p*-xylene compound at 132°/3 mm., melted at 155—157° (Found: C, 66·2; H, 5·1; Br, 18·6%; *M*, 410).

3-*Bromo*-4′ : 4″-*dihydroxy*-3′ : 3″ : 5′ : 5″-*tetramethyltriphenylmethane* was prepared from *m*-bromobenzaldehyde (4·6 g.) and 2 : 6-xylenol (6·6 g.) (48 hr.). The orange product (10 g.) yielded the *benzene compound* in pale yellow crystals which softened at *ca.* 100° with loss of solvent (Found: loss at 100°/4 mm., 16·2. $C_{23}H_{23}O_2Br,C_6H_6$ requires C_6H_6, 16·0%). The unsolvated compound melted at 140—142° (Found: C, 67·4; H, 5·7; Br, 19·5%; *M*, 417. $C_{23}H_{23}O_2Br$ requires C, 67·2; H, 5·6; Br, 19·5%; *M*, 411).

4-*Bromo*-4′ : 4″-*dihydroxytriphenylmethane* was prepared from *p*-bromobenzaldehyde (1·5 g.) and phenol (1·7 g.) (72 hr.). The product (2·5 g.) yielded the *benzene compound* in pale yellow crystals which melted at 98° with loss of solvent (Found: loss at 100°/4 mm., 24·5. $2C_{19}H_{15}O_2Br,3C_6H_6$ requires C_6H_6, 24·8%). The unsolvated compound melted at 124—126° (Found: C, 64·3; H, 4·4; Br, 22·9%; *M*, 397).

4-*Bromo*-4′ : 4″-*dihydroxy*-3′ : 3″ : 5′ : 5″-*tetramethyltriphenylmethane* was prepared from *p*-bromobenzaldehyde (2·3 g.) and 2 : 6-xylenol (3·3 g.) (18 hr.). The product (5 g.) yielded the *benzene compound* as pale orange needles which melted at 156—166° with loss of solvent (Found: loss at 100°/3 mm., 12·0. $3C_{23}H_{23}O_2Br,2C_6H_6$ requires C_6H_6, 11·2%). The unsolvated compound melted at 164—166° (Found: C, 67·3; H, 5·7; Br, 18·0%; *M*, 469).

2-*Bromo*-4′ : 4″-*dihydroxytriphenylmethane* was prepared from *o*-bromobenzaldehyde (2·3 g.) and phenol (2·6 g.) (time, 48 hr.). The benzene compound formed fine, white needles which softened at 120° with loss of solvent; the benzene content was variable and non-stoicheiometric (Found: loss at 100°/3 mm., 15·8; 14·6%). The unsolvated compound melted at 156—157° (Found: C, 65·4; H, 4·3; Br, 21·9%; *M*, 350).

We are grateful to Mr. H. M. Powell for his advice, and for making a preliminary examination of some of the compounds described in the previous paper.[1] One of us (T. F. L.) thanks the University of Hong Kong for a grant.

UNIVERSITY OF HONG KONG, HONG KONG. [*Received, March* 17*th*, 1958.]

655. *Properties and Reactions of Alkyl Free Radicals in Solution. Part XI.* Further Water-soluble Radicals.*

By R. M. Haines and William A. Waters.

In Part VIII[1] we described the preparation and decomposition of azo-nitriles obtained from lævulic and γ-oxopimelic acids, showing that the resulting free radicals had redox potentials E_{-e} of about +0·4 v. Attempts to make further water-soluble alkyl radicals are now reported. All are polymerisation catalysts with similar redox potentials. A more detailed study of the decomposition of azo-nitriles in water gives added support for the finding of Talât-Erben and Bywater[2] that some radical combination to keten-type intermediates $RR'C(CN)\cdot N{:}C{:}CRR'$ occurs, for 13% of an amide $Me_2C(CN)\cdot NH\cdot COPr^i$ has been isolated after decomposition of an aqueous suspension of $\alpha\alpha'$-azo*iso*butyronitrile, the yield of tetramethylsuccinonitrile being substantially less than that reported by Bickel and Waters[3] for the decomposition in toluene.

Experimental.—1 : 1′-*Azobis*-2-*carboxymethyl*-1-*cyano*cyclo*pentanone.* 2-Oxo*cyclo*pentylacetic acid,[4] m. p. 53°, was characterised as the *ethyl ester* 2 : 4-*dinitrophenylhydrazone*, m. p. 107° (Found: C, 51·7; H, 5·1; N, 15·8. $C_{15}H_{18}O_6N_4$ requires C, 51·6; H, 5·2; N, 16·0%). The acid (5·5 g.), neutralised in sodium carbonate solution, was gradually added to stirred sodium cyanide (2 g.) and hydrazine sulphate (2·6 g.) in water (25 ml.), the temperature being kept at 42—45° for 3 hr. The solution was then acidified with hydrochloric acid, cooled in ice, stirred rapidly, and oxidised gradually with bromine. After removal of the slight excess of bromine with sodium hydrogen sulphite the solution was stored at 0° and the solid mixture of isomeric azo-nitriles separated. This, on trituration with ether, gave a white solid, m. p. 156—160° (decomp.), with the requisite absorption spectra for an aliphatic *azo-nitrile* [4·5 (CN), 5·9 μ (CO of CO_2H), and 375 mμ ($\cdot N{:}N\cdot$)] [Found: C, 57·8; H, 6·3; N, 16·3%; equiv., 155. $C_{14}H_{18}N_4(CO_2H)_2$ requires C, 58·0; H, 6·0; N, 16·9%; equiv., 152].

2 : 2′-*Azobis-2-propionamidine dihydrochloride.* Dry hydrogen chloride was passed into $\alpha\alpha'$-azo*iso*butyronitrile (30 g.) in dry methanol (97 ml.) at 0° until the solution was saturated. After 24 hr. the excess of hydrogen chloride was removed under diminished pressure and dry ammonia was passed into the remaining suspension. After a further 2 days' storage at 0° the excess of ammonia was removed similarly. Solid (20 g., m. p. >210°) was separated, dissolved in the minimum volume of cold water, and treated with saturated sodium chloride solution, which precipitated the pure *amidine hydrochloride*, leaving ammonium and sodium chloride in solution. The product was very soluble in water, but insoluble in ether, acetone, or chloroform (Found: C, 35·7; H, 7·8; N, 30·2; Cl, 25·7. $C_8H_{20}N_6Cl_2$ requires C, 35·4; H, 7·4; N, 31·0; Cl, 26·2%), $\lambda_{max.}$ 370 and 210 mμ. The free base was not stable.

2 : 2′-*Azobis-2-butyramidine dihydrochloride*, prepared similarly, in ethanol, from 2 : 2′-azobis-2-cyanobutane[5] (47% yield; decomp. above 200°), had $\lambda_{max.}$ 368 and 211 mμ (Found: C, 39·2; H, 7·9; N, 27·2; Cl, 23·4. $C_{10}H_{24}N_6Cl_2$ requires C, 40·1; H, 8·0; N, 28·1; Cl, 23·7%).

From the decomposition of 2 : 2′-azobis-2-propionamidine hydrochloride (10 g.) in water (60 ml.) at 100° there was obtained a crystalline solid hydrochloride (1·4 g.), m. p. >270° (decomp.) (from moist ethanol), appearing from analyses to be β-*carbamoyl*-$\alpha\alpha\beta$-*trimethylbutyramidine hydrochloride*, $H_2N\cdot CO\cdot CMe_2\cdot CMe_2\cdot C({:}NH)\cdot NH_2,HCl$ (Found: C, 46·6; H, 8·9; N, 20·3; Cl, 16·8. $C_8H_{18}ON_3Cl$ requires C, 46·3; H, 8·7; N, 20·6; Cl, 17·1%); its *picrate*, from ethanol, had m. p. 258—260° (Found: N, 21·4. $C_{14}H_{20}O_8N_6$ requires N, 21·0%). Construction of a scale model of tetramethylsuccindiamidine hydrochloride was found to be spatially impossible: this substance could not be prepared in the normal way from tetramethylsuccinonitrile.

1 : 1′-Azobis-1-cyano-2-oxo*cyclo*pentylacetic acid and both the amidine hydrochlorides

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* Part X, *J.*, 1958, 2056.

[1] Haines and Waters, *J.*, 1955, 4256.

[2] Talât-Erben and Bywater, *J. Amer. Chem. Soc.*, 1955, **77**, 3710, 3712.

[3] Bickel and Waters, *Rec. Trav. chim.*, 1950, **69**, 1490.

[4] Meade and Linstead, *J.*, 1934, 40.

[5] Ford and Waters, *J.*, 1951, 1851.

were, when heated in aqueous solution under nitrogen or carbon dioxide, catalysts for the polymerisations of vinyl cyanide, vinyl acetate, and methyl methacrylate. Their solutions had reducing properties analogous to those of the radicals described in Part VIII.[1] On checking our evidence however, we find that the acid vanadate is not reduced below the oxidation level of blue quadrivalent vanadium.

Attempts have been made to synthesise, from triacetonamine and from aromatic ketones, azo-nitriles containing solubilising groups, *e.g.*, OH, NH_2, NMe_2. This has not been successful but in the course of the work the following new compounds were obtained: the two azo-nitriles were polymerisation catalysts when tested in suspension in hot water.

Storage of 4-*phenylbutan*-2-*one ketazine*, m. p. 40° (Found: C, 82·0; H, 8·2; N, 5·6. $C_{20}H_{24}N_2$ requires C, 82·2; H, 8·3; N, 9·6%), for 2 weeks in moist liquid hydrogen cyanide yielded crystals, m. p. 85—100° of stereoisomers of 3 : 3′-*hydrazobis*-3-*cyano*-1-*phenylbutane* (Found: C, 76·2; H, 7·6; N, 16·1. $C_{22}H_{26}N_4$ requires C, 76·3; H, 7·6; N, 16·2%) which when oxidised, as above, with bromine in dilute hydrochloric acid gave mixed isomers, m. p. 85—95°, of 3 : 3′-*azobis*-3-*cyano*-1-*phenylbutane* in 46% yield (calc. on ketone); a sample crystallised from ethanol had m. p. 110° (Found: C, 76·9; H, 7·5; N, 16·3. $C_{22}H_{24}N_4$ requires C, 76·7; H, 7·0; N, 16·3%). 4-p-*Nitrophenylbutan*-2-*one azine*, m. p. 107—109° (Found: C, 62·2; H, 5·8; N, 14·4. $C_{20}H_{22}O_4N_4$ requires C, 62·8; H, 5·8; N, 14·7%), by a similar procedure gave impure 3 : 3′-azobis-3-cyano-1-*p*-nitrophenylbutane, m. p. 133—135° (decomp.) (Found: C, 61·8; H, 4·8. Calc. for $C_{22}H_{22}O_4N_6$: C, 60·8; H, 5·2%), but at atmospheric pressure addition of more than one molecule of hydrogen cyanide to the ketazines of *p*-hydroxyacetophenone, Michler's ketone, and triacetonamine could not be effected. The *triacetonamine azine*, from light petroleum (b. p. 40—60°), had m. p. 134° (Found: C, 70·7; H, 11·5; N, 18·3. $C_{18}H_{34}N_4$ requires C, 70·6; H, 11·2; N, 18·3%).

Decomposition of αα′-azo*iso*butyronitrile in boiling water has already received brief mention.[6] From 16·4 g. in 200 ml. of water it has been possible to isolate by filtration tetramethylsuccinonitrile, m. p. 169°, in *ca.* 65% yield, and 2 : 3 : 5-tricyano-2 : 3 : 5-trimethylhexane,[3] m. p. 82°, in 7·5% yield. Evaporation of the aqueous solution gave 1·8 g. (13%) of a solid, m. p. 108° (from benzene), that proved to be *N*-(1-cyano-1-methylethyl)*iso*butyramide (Found: C, 62·4; H, 9·2; N, 18·3. Calc. for $C_8H_{14}ON_2$: C, 62·3; H, 9·1; N, 18·1%), identical with material synthesised from α-amino*iso*butyronitrile and *iso*butyryl chloride. The analogous N-(1-*carbamoyl*-3-*carboxy*-1-*methylpropyl*)-γ-*carboxy*-α-*methylbutyramide*, m. p. 150° (from ethanol) (Found: C, 49·3; H, 7·1; N, 9·5. $C_{12}H_{20}O_6N_2$ requires C, 50·0; H, 6·9; N, 9·7%), was isolated in 20% yield on decomposition in water of 4 : 4′-azobis-(4-cyanopentanoic acid).[1] Its infrared spectrum had bands at 2·8—4·0 (OH), 2·9 and 3·0 (NH), 5·9 (CO of CO_2H), 6·1 and 6·35 μ (CO or $CO{\cdot}NH_2$), and 6·6 μ (CO of ·CO·NH·).

One of us (R. M. H.) thanks the Department of Scientific and Industrial Research for a maintenance grant.

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[*Received, March* 26*th*, 1958.]

[6] Tilney-Bassett and Waters, *J.*, 1957, 3129.

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656. *Hydrogenation of* 4-*Hydroxy*iso*phthalic Acid.*

By A. S. LINDSEY.

AN examination of the products of hydrogenation of 4-hydroxy*iso*phthalic acid was made as part of a study of the chemistry [1] and pharmacology of this compound.[2]

Preliminary experiments indicated that hydrogenation of diethyl 4-hydroxy*iso*phthalate over palladium [3] gave low yields. However hydrogenation of the alkali-metal salt in aqueous solution in the presence of Raney nickel catalyst [4] proceeded to approximately 70% completion.

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[1] Hunt, Jones, and Lindsey, *J.*, 1956, 3099; Gladych, Lindsey, and Taylor, *J.*, 1957, 4834.

[2] Chesher, Collier, Robinson, Taylor, Hunt, Jones, and Lindsey, *Nature*, 1955, **175**, 206; Collier and Chesher, *Brit. J. Pharmacol.*, 1956, **11**, 20.

[3] Martin and Robinson, *J.*, 1943, 491.

[4] B.P. 353,373/1931: B.P. 366,244/1932.

One of the products, isolated in about 16% yield, was the previously unknown crystalline 4-hydroxy*cyclo*hexane-1 : 3-dicarboxylic acid, which was characterised by its infrared absorption spectrum and as its dimethyl ester. The non-crystalline portion of the hydrogenation product furnished *trans*-4-hydroxy*cyclo*hexanecarboxylic acid [5,6] and a *cyclo*hexene-1 : 3-dicarboxylic acid, which could also be obtained by treatment of the dimethyl 4-toluene-*p*-sulphonyl*cyclo*hexane-1 : 3-dicarboxylate with potassium *tert.*-butoxide in *tert.*-butyl alcohol and subsequent hydrolysis. The dicarboxylic acid is most likely to be the alkali-stable Δ^3-isomer (m. p. 244°) [7] and must arise through dehydration during either the hydrogenation or distillation.

Experimental.—General. Microanalyses were carried out by the microanalytical section of this laboratory. Infrared absorption spectra of solids dispersed in potassium chloride discs were measured on a modified Hilger D209 double-beam instrument; only the strong and medium strength bands are reported.

Preliminary Hydrogenation Experiments.—Attempts to hydrogenate diethyl 4-hydroxy*iso*phthalate, dissolved in redistilled ethyl acetate, under the following conditions led to the recovery of approximately 90% of the starting material: (*a*) with 5% Pd on asbestos at 155—170° for 7 hr. under 136 atm. of hydrogen, (*b*) with 2% Pd on barium carbonate at 150—200° for 7 hr., under 125 atm. of hydrogen.

Hydrogenation of 4-*Hydroxy*iso*phthalic Acid over Raney Nickel.*—A stirred solution of 4-hydroxy*iso*phthalic acid (100 g.) in sodium hydroxide (73 g. in 600 ml. of water) and W6 Raney nickel (20 g.) [8] were preheated to 140—150° for 3 hr., and then kept at that temperature for 3·7 hr. with a hydrogen pressure of 150 atm. Approximately 50 l. of hydrogen were absorbed (theory, 36 l.). Removal of the catalyst and acidification of the solution with hydrochloric acid precipitated 4-hydroxy*iso*phthalic acid (24 g.), m. p. 300° (decomp.), confirmed by mixed m. p. determination. Saturation of the acid filtrate with ammonium sulphate and continuous extraction with ether led to recovery of the hydrogenated products (67·2 g.). From the ethereal extracts there crystallised 4-*hydroxy*cyclo*hexane*-1 : 3-*dicarboxylic acid* (16·5 g.), m. p. 188° (from ether) (Found: C, 51·1; H, 6·5%; equiv., 94·5. $C_8H_{12}O_5$ requires C, 51·1; H, 6·4%; equiv., 94·1). Infrared absorption spectrum: 3384, 3230, 2942, 2875 (sh), 2630, 2550 (sh), 1722, 1693, 1451, 1426, 1415, 1309, 1283, 1248, 1227, 1193, 1055, 1042 cm.$^{-1}$.

Fischer–Speier esterification with methanol gave the *dimethyl ester*, b. p. 170—173°/20 mm., n_D^{21} 1·4725 (Found: C, 55·1; H, 7·3. $C_{10}H_{16}O_5$ requires C, 55·5; H, 7·5%).

Esterification of the Hydrogenation Products.—The ether-soluble hydrogenation products (50·7 g.) recovered from solution, after filtration of the hydroxy*cyclo*hexanedicarboxylic acid, were esterified with ethanol and hydrochloric acid. Working up in the usual way gave acid products (9 g.), and neutral esters (54 g.) which were distilled at reduced pressure to give the following fractions: (1) b. p. <115°/1 mm.; (2) b. p. 115—118°/1 mm. (13·0 g.), n_D^{21} 1·4615; (3) b. p. 118—137°/1 mm. (12·9 g.), n_D^{21} 1·4611; residue (16·5 g.).

Examination of Fraction 2.—Hydrolysis with hot sodium hydroxide, acidification, saturation with salt, and continuous extraction with ether gave 4-hydroxy*cyclo*hexanecarboxylic acid, which recrystallised from ether–light petroleum (b. p. 60—80°) and ethyl acetate–light petroleum (b. p. 60—80°) as needles, m. p. 149—150° (Found: C, 58·6; H, 8·2. Calc. for $C_7H_{12}O_3$: C, 58·3; H, 8·4%), giving no coloration with ferric chloride solution. Infrared absorption spectrum: 3450, 2940, 2867, 2700, 2596, 1705, 1451, 1366, 1336, 1309, 1232, 1200, 1056, 1030, 982, 974, 947, 785 cm.$^{-1}$. Admixture with *trans*-4-hydroxy*cyclo*hexanecarboxylic acid [6] did not depress the m. p.; admixture with the *cis*-compound did.

Treatment of the hydroxy-acid with acetic anhydride in pyridine at room temperature furnished the *trans*-monoacetate, m. p. and mixed m. p. 135—136° (Found: C, 57·7; H, 7·6. Calc. for $C_9H_{14}O_4$: C, 58·05; H, 7·6%).

Oxidation of Ethyl trans-4-*Hydroxy*cyclo*hexanecarboxylate.*—*trans*-4-Hydroxy*cyclo*hexanecarboxylic acid (250 mg.) was converted into the ethyl ester by the Fischer–Speier method, and the oily product, in acetic acid (5 ml.), treated with chromium trioxide (120 mgm.) in acetic acid

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[5] Campbell and Hunt, *J.*, 1950, 1379.

[6] We are greatly indebted to Drs. Campbell and Hunt for samples of the *cis*- and *trans*-4-hydroxy- and *trans*-4-acetoxy-*cyclo*hexanecarboxylic acids.

[7] Farmer and Richardson, *J.*, 1927, 59; Kon and Nandi, *J.*, 1933, 1628.

[8] Adkins and Billica, *J. Amer. Chem. Soc.*, 1948, **70**, 695.

(4 ml.) and water (1 ml.) for 48 hr. at room temperature. Recovery in the usual way gave an oil, which showed no coloration with ferric chloride solution (absence of a 2-keto-ester). The ethyl 4-oxo*cyclo*hexanecarboxylate readily furnished the 2 : 4-*dinitrophenylhydrazone*, orange needles (from ethanol), m. p. 125—126° (Found: C, 51·4; H, 5·2; N, 15·9. $C_{15}H_{18}O_6N_4$ requires C, 51·4; H, 5·1; N, 16·0%).

Examination of the Residue.—Treatment of the residue with ether gave a little unchanged 4-hydroxy*iso*phthalic acid. The recovered non-crystallisable material in ethanol (10 ml.) was refluxed with 20% sodium hydroxide solution (100 ml.). After removal of a little non-hydrolysed material with ether, acidification and continuous extraction with ether gave a viscous oil which slowly crystallised. Recrystallisation from ether–light petroleum (b. p. 40—60°) gave a *cyclo*hexene-1 : 3-dicarboxylic acid, m. p. 248—249° (Found: C, 56·5; H, 5·9%; equiv., 87. Calc. for $C_8H_{10}O_4$: C, 56·5; H, 5·9%; equiv., 85), giving a yellow coloration with ethereal tetranitromethane and none in the Liebermann–Burchard reaction. Infrared absorption spectrum: 2880, 2848, 2595, 2530, 1680, 1641, 1417, 1270, 1201, 950, 934, 745, 701 cm.$^{-1}$.

Preparation of cyclo*Hexene*-1 : 3-*dicarboxylic Acid.*—Dimethyl 4-hydroxy*cyclo*hexane-1 : 3-dicarboxylate (2 g.) was refluxed with toluene-*p*-sulphonyl chloride (2 g.) in anhydrous pyridine (15 ml.) for 2 hr., poured into dilute hydrochloric acid, and continuously extracted with ether. After benzene had been added, the solution was washed with sodium hydrogen carbonate solution and water, and dried (Na_2CO_3). Solvents were removed and the toluenesulphonate was refluxed with potassium *tert.*-butoxide in *tert.*-butyl alcohol (1·5 hr.). Water was then added and refluxing continued (1 hr.). Acidification with hydrochloric acid, and recovery with ether gave an oil which partly crystallised. Recrystallisation of these crystals from ether–light petroleum (b. p. 60—80°) gave a methyl hydrogen 4-*toluene*-p-*sulphonyl*cyclo*hexanecarboxylate*, m. p. 130—131° (Found: C, 53·9; H, 5·6; S, 9·6. $C_{16}H_{20}O_7S$ requires C, 53·9; H, 5·7; S, 9·0%).

The non-crystallisable oil was again refluxed (6 hr.) with potassium *tert.*-butoxide in *tert.*-butyl alcohol, then water added and refluxing continued (5 hr.). Working up as before and recrystallisation from ether–light petroleum (b. p. 60—80°) gave the same *cyclo*hexenedicarboxylic acid as that isolated from the residue of the hydrogenation (mixed m. p. and infrared spectrum).

We thank Mr. W. Kynaston for measurement of infrared spectra, and Monsanto Chemicals Ltd. for gifts of 4-hydroxy*iso*phthalic acid. The work described formed part of the programme of this Laboratory.

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[*Received, April 17th*, 1958.]

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657. *The Solubility of Anhydrous Aluminium Bromide in Pent-2-ene.*

By FRED FAIRBROTHER and JOHN F. NIXON.

THE solubility of aluminium bromide has already been measured in a number of inorganic and organic solvents,[1,2,3] including saturated and aromatic hydrocarbons and their derivatives, but not an olefin. Such measurements, however, are of special interest in view of the polymerisation of most olefins in the presence of Friedel–Crafts-type catalysts, a circumstance which renders such solubility measurements very difficult.

With many olefins examined,[4] it has not been found possible to prevent this polymerisation in the presence of aluminium bromide, even with rigorous exclusion of air and moisture. This may be a matter of degree, and possibly the small amount of moisture released when even well out-gassed Pyrex glass is sealed off, is sufficient to initiate polymerisation. However, by careful drying and pre-treatment of the solvent with aluminium

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[1] Heldmann and Thurmond, *J. Amer. Chem. Soc.*, 1944, **66**, 427.
[2] Boedeker and Oblad, *ibid.*, 1947, **69**, 2036.
[3] Eley and King, *Trans. Faraday Soc.*, 1951, **47**, 1287.
[4] Fairbrother and Field, *J.*, 1956, 2614.

bromide, a stable solution of aluminium bromide in pent-2-ene can be prepared. Its ultraviolet absorption gave evidence of the existence of some solvent–solute complex formation. Its vapour pressure was consistent with a weak aluminium bromide dimer–solvent association in concentrated solution, but gave no evidence, down to −23°, of the formation of any solid complex. A solution of aluminium bromide in pent-2-ene, containing 0·017 mole of Al_2Br_6 per litre, and sealed in a quartz absorption cell, has remained without any visible change for more than two years.

Since evidence of complex formation in solution can sometimes be obtained from solubility measurements, we have now measured the solubility of aluminium bromide in pent-2-ene from about 20° to −10°. Among the recorded solubilities of aluminium bromide those most relevant are in benzene, *n*-butane, and *n*-hexane, all of which have been measured by the disappearing-crystal method. The solubility parameter δ of *n*-butane is 6·7 and that of *n*-hexane 7·30.[5] The solubility parameter of pent-2-ene can be calculated approximately from Hildebrand and Scott's equation[5] $\delta = [(\Delta H^V - \boldsymbol{R}T)/V^e]^{\frac{1}{2}}$. Using the heat of vaporisation (ΔH^V) calculated by the Clausius–Clapeyron equation from the vapour-pressure data of Scott and Waddington,[6] and the molar volume V^e derived from published density data,[7] we obtain a value for δ of 7·4.

The solubilities in *n*-butane and in *n*-hexane are both well below the ideal but show fair agreement with the equation for regular solutions. Accordingly the solubility (mole fraction) is slightly greater, especially at the lower temperatures, in *n*-hexane than in *n*-butane. The highest temperature used in the present work (21·1°) is below the lowest used for the solubilities in benzene (28·2°), *n*-butane (28·3°), or *n*-hexane (30·6°), but very short extrapolation of the log x_1–$1/T$ curves enables a comparison to be made at a common temperature of 25°. One would expect, from a consideration of the respective solubility parameters of the solvents, that the solubility of aluminium bromide in pent-2-ene would be only slightly greater than that in *n*-hexane, which in turn, on a mole-fraction basis, is about 25% greater at 25° than the solubility in *n*-butane. On the other hand, the curves show that at this temperature the solubility in pent-2-ene is about 2·2 times that in *n*-hexane, 2·75 times that in *n*-butane, but only about 25% less than that in benzene, which has a solubility parameter of 9·15 and which forms a solid complex at this temperature melting incongruently at 37°. This confirms that a weak complex formation exists in solution between aluminium bromide and pent-2-ene.

Experimental.—Pent-2-ene. Commercial pent-2-ene was dried over sodium wire and fractionated. The fraction with b. p. 35·8°/749 mm. was collected and stored over bright sodium wire. Infrared absorption showed that it consisted mainly of the *cis-* and the *trans-*isomers in roughly equal amount.

Aluminium bromide. This was prepared from dry bromine and pure aluminium wire, purified by four vacuum-sublimations, and stored in fragile hook-ended ampoules.

Solubilities were measured in a closed system as described by Fairbrother, Scott, and Prophet.[8] The Table gives the solubilities (*s*) as g. of aluminium bromide dissolved by 100 g. of pent-2-ene and the Figure shows the log mole fraction of solute (x_1) as a function of $1/T$ (°K).

	Run 2						Run 3				
Temp. (°)	21·1	17·2	11·7	5·8	−3·0	−11·2	20·9	17·5	12·7	2·0	−3·7
s	77·78	69·04	60·15	53·08	42·92	37·31	75·19	66·71	64·80	43·90	38·39

For the first run the dried pent-2-ene was pre-treated four times with pure aluminium bromide during which decreasing amounts of polymerisation occurred. When the aluminium bromide and pent-2-ene had been transferred to the solubility cell and allowed to stand, it was evident that some polymerisation had occurred, from both the colour and the separation of small amounts of a viscous liquid, which appeared to block the sintered filter. Nevertheless a series of solubility measurements were made with this solution. These are recorded as Run 1

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[5] Hildebrand and Scott, " The Solubility of Non-electrolytes," Reinhold, New York, 1950.

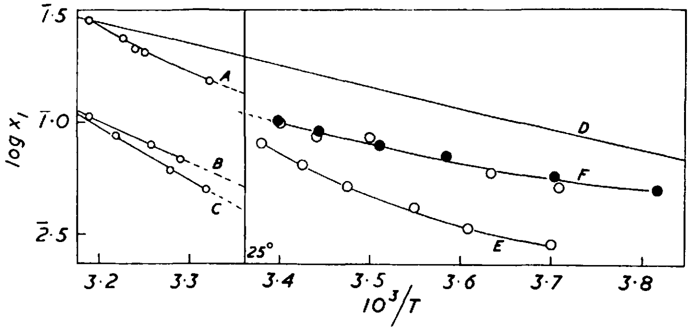
[6] Scott and Waddington, *J. Amer. Chem. Soc.*, 1950, 4311.

[7] National Bureau of Standards, Circular 461, 1947, 46.

[8] Fairbrother, Scott, and Prophet, *J.*, 1956, 1164.

(curve *E*) on Fig. 1 and show how the presence of polymer reduces the solubility. This polymerisation could have been due to liberation of moisture from the glass during sealing off or to unremoved traces of hydrogen bromide formed during the pre-treatments; dry hydrogen bromide brings about polymerisation.

The pent-2-ene was therefore, for Run 2, further pre-treated with aluminium bromide and for Run 3 once more; in each case a greater proportion of the pent-2-ene was sacrificed in order to sweep away hydrogen bromide that might have been formed. The consistency of the results for Runs 2 and 3 (curve *F*, black and open circles respectively) shows that the effect of pre-treatment has reached a limit.



After Run 2 a small amount of the solvent was distilled from the residual aluminium bromide: infrared absorption showed that it had the same composition as the starting material.

The Figure also gives a number of published solubilities in (*A*) benzene,[3] (*B*) *n*-hexane,[2] and (C) *n*-butane [1] and (*D*) the ideal solubility calculated by Hildebrand and Scott's equation [6] by use of data quoted by Eley and King.[3]

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[*Received, April 24th,* 1958.]

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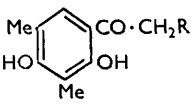
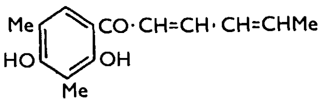
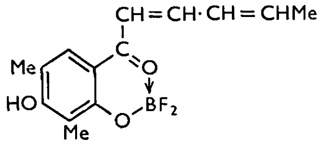
658. *A New Synthesis of Clavatol and of Sorbicillin.*

By J. F. W. McOMIE and M. S. TUTE.

CLAVATOL, isolated from cultures of *Aspergillus clavatus*,[1] has been shown to be 2 : 4-dihydroxy-3 : 5-dimethylacetophenone (I; R = H) by Hassal and Todd,[2] who synthesised it in 68% yield by a Hoesch reaction of methyl cyanide with 2 : 4-dimethylresorcinol. Clavatol has now been synthesised in high yield by acetylation of 2 : 4-dimethylresorcinol with the commercially obtainable solution of boron trifluoride in acetic acid.


(I)


(II)


(III)

The closely related compound, sorbicillin (II), was isolated during the purification of clinical penicillin,[3] and its structure was elucidated by Cram.[4] The structure (II) was confirmed by Kuhn and Staab [5] who converted 2 : 4-dimethylresorcinol into ω-chloro-2 : 4-dihydroxy-3 : 5-dimethylacetophenone (I; R = Cl) and then carried out a

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[1] Bergel, Moss, Morrison, and Rinderknecht, *J.*, 1944, 417.
[2] Hassal and Todd, *J.*, 1947, 611.
[3] Cram and Tishler, *J. Amer. Chem. Soc.*, 1948, **70**, 4238.
[4] Cram, *ibid.*, p. 4240.
[5] Kuhn and Staab, *Chem. Ber.*, 1954, **87**, 266.

Reformatsky reaction with crotonaldehyde. In this way a minute yield of sorbicillin (0·26%) was obtained, the main product being clavatol (I; R = H). Interaction of sorbic acid and 2 : 4-dimethylresorcinol in presence of boron trifluoride in ether gives a compound, $C_{14}H_{15}O_3BF_2,H_2O$, which is considered to be the monohydrate of compound (III). A similar formulation has been given to the product obtained from boron trifluoride and 2-hydroxy-3 : 5-dimethylacetophenone.[6] Attempted recrystallisation of the hydrate from aqueous methanol gave sorbicillin (II). Cram and Tishler [3, 4] described this compound as an orange solid whereas Kuhn and Staab [5] stated that their product was yellow. This is clearly an example of polymorphism and we have obtained sorbicillin in both forms.

Experimental.—Commercial 2 : 4-dimethylresorcinol[7] was recrystallised from petroleum (b. p. 60—80°).

Clavatol (I; R = H). 2 : 4-Dimethylresorcinol (3·0 g.) and commercial boron trifluoride–acetic acid complex (5 ml.) were warmed on a water-bath for 3 hr. The mixture, after dilution with water (50 ml.) and addition of concentrated hydrochloric acid (3 ml.), was boiled for 1 min., then cooled and the product was collected. Recrystallisation (charcoal) from methanol gave clavatol (3·2 g., 93%) as needles, m. p. 178—180°, raised by further crystallisation to 182—184° (lit.,[3] m. p. 183°) (Found: C, 66·8; H, 6·7. Calc. for $C_{10}H_{12}O_3$: C, 66·7; H, 6·7%). The acetate, twice recrystallised from aqueous methanol, had m. p. 96—97° (lit.,[3] m. p. 95—96°) (Found: C, 65·1; H, 6·2. Calc. for $C_{12}H_{14}O_4$: C, 65·0; H, 6·3%).

Sorbicillin (II). 2 : 4-Dimethylresorcinol (3·0 g.), sorbic acid (2·44 g.), and 45% boron trifluoride in ether (7 ml.) were warmed on a water-bath for 3 hr. After the addition of water (50 ml.) and concentrated hydrochloric acid (3 ml.), the mixture was warmed at 80° for 5 min. The solution was decanted from a viscous, red material which was well washed by decantation, then triturated with ether (100 ml.), thereby giving a bright orange solid (2·08 g.), m. p. 224—225° (Found: C, 56·4; H, 5·9; F, 12·9. $C_{14}H_{15}O_3BF_2,H_2O$ requires C, 56·4; H, 5·7; F, 12·75%). The presence of boron was shown by a green flame when a solution of the substance in ethanol–sulphuric acid was ignited. When the solid was boiled with aqueous methanol, the resulting solution deposited sorbicillin as yellow plates (1·55 g., 33%) which after one recrystallisation had m. p. 112—114° (the melt became solid and melted again at 127—143°; lit.,[3] 113—114° and 129—130°) (Found: C, 72·3; H, 7·1. Calc. for $C_{14}H_{16}O_3$: C, 72·4; H, 6·9%).

The ether filtrate (see above) was extracted with aqueous sodium carbonate which was then acidified, giving a brown solid (0·95 g., 20%). Two recrystallisations from aqueous methanol gave orange crystals of sorbicillin, m. p. 111° (with partial melting, resolidification, and remelting over a range 122—135° depending on rate of heating). A mixed m. p. with the yellow form showed no depression and, when a saturated solution of the orange form was seeded with a crystal of the yellow form, the solution deposited yellow plates. The orange and the yellow form gave the same acetate, m. p. 103—104° (lit.,[4] 103—104°) (Found: C, 70·1; H, 6·4. Calc. for $C_{16}H_{18}O_4$: C, 70·0; H, 6·5%). In ethanol the two forms gave absorption spectra which were almost identical with each other and with that recorded [3] for the orange form. Sorbicillin and its acetate gave a black colour with ferric chloride as previously noted.[4]

The authors are grateful to Dr. A. M. G. MacDonald for the fluorine analysis.

THE UNIVERSITY, BRISTOL. [*Received, April 28th*, 1958.]

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[6] Kästner, "Newer Methods of Preparative Organic Chemistry," Interscience Publ. Inc., New York, 1948, p. 282.

[7] Baker, Bondy, McOmie, and Tunnicliff, *J.*, 1949, 2834.

659. *Polyenealdehydes as Proton Acceptors.*

By Albert Wassermann.

It has been shown[1] that ω-*p*-methoxyphenylpolyenealdehydes are proton acceptors. Oxygen is more electronegative than carbon and it is probable therefore that oxygen, rather than carbon, is protonated in these reactions. In order to find out whether the oxygen atom of the methoxy- or of the aldehyde group is involved, some properties of protonated 5-phenyl-2 : 4-pentadienal were determined and they are compared, in the Table, with those of ω-*p*-methoxyphenyl-2 : 4-pentadienal.[1] In both sets of measurements the proton-donor was trichloroacetic acid and the solvent benzene, and the experimental technique was the same (temp. 20° unless otherwise stated). The figures show that the proton-acceptor properties of the two polyenealdehydes are similar, so it is concluded that the proton is taken up by the carbonyl-oxygen atom.

		5-Phenyl-2 : 4-pentadienal *	ω-(*p*-Methoxyphenyl)-2 : 4-pentadienal
Light absorption max. (mμ)	No acid	320	350
	1·00M in $CCl_3{\cdot}CO_2H$	350	380
Increment due to proton transfer (mμ)		30	30
Max. molar light absorption coeff., $10^5\varepsilon_{max.}$ (l. mole^{-1} cm.$^{-1}$)	No acid	0·38	0·35
	1·00M in $CCl_3{\cdot}CO_2H$	0·35	0·30
Equil. coeff., *K* (l. mole^{-1}), for proton-transfer from $CCl_3{\cdot}CO_2H$ to aldehyde		30 ± 4	30 ± 4
Mol. electr. conductance of protonated species, $\Lambda \times 10^7$ (l. mole^{-1} ohm^{-1} cm.$^{-1}$); soln. 1·00M in $CCl_3{\cdot}CO_2H$, 1·00 × 10^{-4}M in aldehyde at 25°		2·5 ± 0·5	1·8 ± 0·3
Reversibility test with dioxan (cf. Fig. 5, ref. 1)		+	+

* Kindly placed at our disposal by Dr. M. C. Whiting; b. p. 158°/3 mm. (in nitrogen).

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[1] Wassermann, *J.*, 1958, 1014.

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660. *Deuteration of Glyoxaline studied by Nuclear Magnetic Resonance.*

By R. J. Gillespie, A. Grimison, J. H. Ridd, and R. F. M. White.

The orientation of electrophilic substitution in glyoxaline appears to depend on the reagent;[1] nitration and sulphonation occur at the 4(or 5)-position, and diazo-coupling occurs at the 2-position. It has been suggested that this change in orientation arises because diazo-coupling involves the conjugate base of glyoxaline, while nitration and sulphonation involve the neutral molecule or the conjugate acid.[2] It was therefore of interest to determine whether the orientation of a given substitution could be changed by an alteration in the pH of the medium. Such a change is here reported for the deuteration of glyoxaline.

In D_2O alone, deuteration occurs initially in the 4 : 5-positions, and in sodium deuteroxide solution it occurs initially in the 2-position. This conclusion is supported by preliminary kinetic studies on the rate of deuteration.

Experimental.—A 4% solution of glyoxaline in D_2O was heated for 4 hr. at 250°; the D_2O was distilled off, and the glyoxaline purified by sublimation *in vacuo*. The proton nuclear magnetic resonance spectrum of a 40% solution of the product (*A*) in D_2O was then measured on a Varian Associates V-4300 high-resolution spectrometer at 40 Mc./sec., in a 5 mm. o.d.

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[1] Schofield, *Quart. Reviews*, 1950, **4**, 382.

[2] R. D. Brown, Duffin, Maynard, and Ridd, *J.*, 1953, 3937.

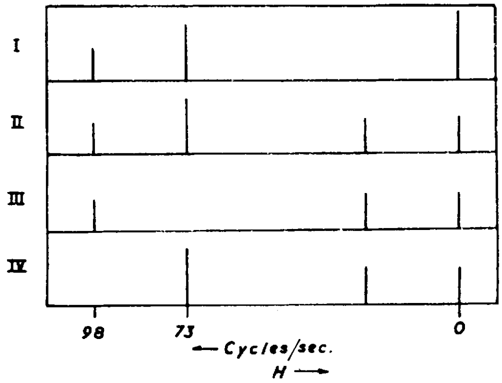
sample tube with an internal capillary of water to provide a reference signal. The spectrum obtained is shown diagrammatically (III) in the Figure.

A 5% solution of glyoxaline in D_2O containing NaOD (1·3M) was heated for 2 hr. at 150°; the product was extracted and purified as above. The nuclear magnetic resonance spectrum of a 40% solution of the product (*B*) in D_2O is also shown (IV) in the Figure.

By submitting a further sample of glyoxaline to both the above treatments, a product (*C*) was obtained, and its nuclear magnetic resonance spectrum in a 40% solution in D_2O was measured.

The nuclear magnetic resonance spectrum of a 40% solution of glyoxaline in H_2O (I) consists of two lines with an intensity ratio of 2 : 1 shifted by 73 and 98 c./sec. respectively from the intense line of the solvent. These lines can be identified with the two protons in the 4 : 5-positions and the single proton in the 2-position respectively. The proton on the 1-nitrogen atom exchanges rapidly with the solvent and also with the 3-position and therefore does not give rise to a separate line. This exchange also means that the protons in the 4- and the 5-position are equivalent and therefore only give rise to one line as observed. In a 40% solution in D_2O, the same spectrum is observed (II) except that the solvent line is replaced by the line due to the reference sample of water in the internal capillary tube, and a fourth line appears owing to the protons on the 1-position and the HDO molecules formed by exchange.

Proton nuclear magnetic resonance spectrum of glyoxaline (I, II), 4 : 5-*dideuteroglyoxaline* (III), *and* 2-*deuteroglyoxaline* (IV).



The spectrum of the product *A* in D_2O contains the line at 98 c./sec. due to the proton in the 2-position, the line due to the proton in the 1-position (introduced during preliminary experiments in H_2O), and the reference line, but no line at 73 c./sec. due to the protons in the 4- and the 5-position. Thus it must be 4 : 5-dideuteroglyoxaline. On the other hand, the spectrum of the product *B* contains the line at 73 c/.sec. but no line at 98 c./sec.; it must therefore be 2-deuteroglyoxaline. The product *C* gives no line at either 73 or 98 c./sec. and is therefore 2 : 4 : 5-trideuteroglyoxaline.

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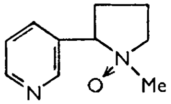
[*Received, April* 29*th*, 1958.]

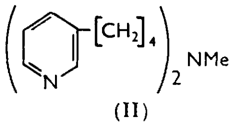
661. *New Transformation Products of Nicotine.*

By A. W. Johnson, T. J. King, and J. R. Turner.

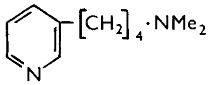
Of the three possible *N*-oxides of nicotine only the mono-*N*-oxide (I) has been prepared previously.[1] It has now been found that oxidation of nicotine in acetic acid with hydrogen peroxide gives the di-*N*-oxide as a yellow hygroscopic oil, characterised by the formation of a monopicrate. Reduction of the di-*N*-oxide with sulphur dioxide gives the *ar*-mono-*N*-oxide (dipicrate, monopicrolonate): further reduction re-forms nicotine itself. Attempts to nitrate or mercurate nicotine *ar*-mono-*N*-oxide were uniformly unsuccessful.



(I)



(II)



(III)

During a dehydrogenation of nicotine to nicotyrine,[2] a higher-boiling fraction was formed which has been formulated as *N*-methyl di-(4-3′-pyridylbutyl)amine (II) on the grounds of its physical properties and its decomposition by the Hofmann reaction to *NN*-dimethyl-4-3′-pyridylbutylamine (III) (characterised as its dipicrolonate). The base (III) has been synthesised by methylation of dihydrometanicotine (*N*-methyl-4-3′-pyridylbutylamine) with methyl iodide and the product identified with that obtained in the earlier experiment. The other compound, presumably 3-but-3′-enylpyridine, from the Hofmann degradation, was not isolated.

Experimental.—*Nicotine di-*N*-oxide monopicrate.* 30% Hydrogen peroxide (100 c.c.) was added to nicotine (redistilled; 40 c.c.) in glacial acetic acid (300 c.c.) and the mixture heated at 70°. After 3 hr. more hydrogen peroxide (100 c.c.) was added and the heating was continued for 8½ hr. The volume of the mixture was reduced to *ca.* 200 c.c. by distillation at the water-pump, distilled water (100 c.c.) was added, and the volume then reduced to 150 c.c. This process was repeated twice in order to remove all excess of hydrogen peroxide and peracetic acid; failure to observe this precaution may lead to a violent explosion. The volume of the mixture was finally reduced to *ca.* 100 c.c. and the clear yellow viscous residue was cooled and treated in a large beaker with excess of anhydrous sodium carbonate. The free base was extracted from the resulting paste with hot ethanol (3 × 200 c.c.) or chloroform (3 × 200 c.c.). Removal of the solvent then gave the oxide (45 g.; 92%) as a clear yellow, viscous hygroscopic oil. The *picrate*, prepared in ethanol, was triturated with acetone and crystallised from water: it decomposed above 220° (Found: C, 45·5; H, 4·0; N, 16·5. $C_{16}H_{17}O_9N_5$ requires C, 45·4; H, 4·05; N, 16·55%).

Nicotine ar-*mono-*N*-oxide.* The di-*N*-oxide of nicotine prepared in the previous experiment was dissolved in ethanol (200 c.c.) and the solution saturated with sulphur dioxide.[3] The colour of the reaction mixture quickly deepened to dark red and heat was evolved. The solution was cooled and kept overnight, after which the solvent was evaporated under reduced pressure. More alcohol (200 c.c.) was added and again removed in order to ensure complete removal of the sulphur dioxide. The resulting thick red oil was made alkaline by an excess of sodium carbonate and the mixture then extracted repeatedly with chloroform (3 × 100 c.c.). Removal of the solvent from the dried red solution gave a light red oil (32 g.). Small quantities were distilled at 90—110° (air-bath)/5×10^{-5} mm. The viscous, pale yellow, highly refractive, hygroscopic oil so obtained was sealed *in vacuo* before analysis (Found: C, 66·8; H, 7·7; N, 15·6. $C_{10}H_{14}ON_2$ requires C, 67·4; H, 7·9; N, 15·7%). Exposure to air caused the rapid formation of a red colour. The *dipicrate*, prepared in hot aqueous solution from the distilled product, formed fine yellow needles, m. p. 147—148° (Found: C, 41·7; H, 3·45; N, 17·8. $C_{22}H_{20}O_{15}N_8$ requires C, 41·5; H, 3·2; N, 17·6%). The *monopicrolonate* was formed from the distilled

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[1] Pinner, *Ber.*, 1895, **28**, 456.

[2] Frank, Holley, and Wikholm, *J. Amer. Chem. Soc.*, 1942, **64**, 2835.

[3] Ochiai, *J. Org. Chem.*, 1953, **18**, 534.

product in acetone solution; it formed pale yellow crystals, m. p. 190—191° (Found: C, 54·5; H, 5·3; N, 18·6. $C_{20}H_{22}O_6N_6$ requires C, 54·3; H, 5·0; N, 19·0%).

For the preparation of this mono-*N*-oxide it is unnecessary to isolate the di-*N*-oxide; when the crude alcoholic solution of the di-*N*-oxide was reduced directly with sulphur dioxide yields of up to 92% of the mono-*N*-oxide (based on nicotine) before distillation were obtained.

Reduction of nicotine ar-*mono*-N-*oxide*. The oxide (redistilled; 1 g.) was heated under reflux in acetic acid (30 c.c.) in the presence of grease-free iron powder (2·2 g.) for 75 min. The solution was basified by excess of solid potassium hydroxide, and the product distilled in steam. The clear distillate gave a picrate which had m. p. 218° after crystallisation from water. The m. p. was not depressed on admixture with authentic nicotine picrate, m. p. 218°.

N-*Methyldi*-4-3′-*pyridylbutylamine* (II). Nicotine (150 g.) was dehydrogenated over palladium–asbestos at 230° rising to 280° (cf. Frank *et al.*[2]). After removal of nicotyrine (13 g.), b. p. 92—94°/0·1 mm., from the product, a second fraction (34 g.), b. p. 190—192°/0·1 mm., was obtained as a pale yellow oil. This *amine* was redistilled and the fraction (30 g.), b. p. 198—200°/0·3 mm., was collected: it had n_D^{20} 1·5411 [Found: C, 77·4; H, 8·8; N, 14·2%; *M* (Rast), 308. $C_{19}H_{27}N_3$ requires C, 76·7; H, 9·15; N, 14·15%; *M*, 297], $\lambda_{max.}$ (in 95% EtOH) 257, 263, and 269 mμ (log ε 3·77, 3·82, and 3·69 respectively). The infrared spectrum revealed no maxima between 3400 and 3200 cm.$^{-1}$, confirming the absence of $>$NH. The base was soluble in ethanol and acetone but insoluble in water. Potentiometric titration of a solution in 20% ethanol against 0·1N-hydrochloric acid revealed two basic groups, p*K*′ 5·7 and 9·15 respectively.

NN-*Dimethyl*-4-3′-*pyridylbutylamine*. (i) The base (6·2 g.) from the foregoing experiment was mixed at room temperature and kept with methyl iodide (2·9 g.) in acetone (12 c.c.) for 1½ hr. The mixture was cooled and shaken at room temperature overnight with a suspension of silver oxide prepared from aqueous silver nitrate (3·8 g.) and sodium hydroxide (2·0 g.). The solid material was filtered off and the aqueous solvent removed at reduced pressure. The residual brown gum was heated (oil-bath) and decomposition which commenced at 155° became vigorous at 160°. The resulting brown oil was extracted into ether, dried, and recovered. The residue was distilled from a bulb tube and the fraction, b. p. 130—132°/16 mm. (bath-temp.), was collected as a colourless oil which darkened rapidly in air although it could be preserved *in vacuo*. The *dipicrolonate* formed yellow plates, m. p. 208—210°, from aqueous methanol (Found: C, 53·0; H, 5·0; N, 19·5. $C_{31}H_{34}O_{10}N_{10}$ requires C, 52·7; H, 4·85; N, 19·8%).

(ii) Dihydrometanicotine (5·7 g.; see below) was heated with methyl iodide (4·9 g.) in ethanol (15 c.c.) under reflux on the water-bath for 1 hr. An alcoholic solution of potassium hydroxide (2·5 g.) was added and the heating continued for a further ½ hr. After cooling, the precipitated potassium iodide was separated and most of the alcohol removed under reduced pressure. Water (20 c.c.) was added to the residue and the solvent again removed. 5N-Aqueous sodium hydroxide (20 c.c.) was added and the brown oil which formed on the surface of the solution was extracted with chloroform (2 × 100 c.c.). Removal of the solvent from the dried extract gave a brown oil which was distilled and the fraction, b. p. 93—94°/1 mm. (5·2 g.), n_D 1·5030, was collected. The dipicrolonate had m. p. 208—210° not depressed on admixture with the product from the previous experiment.

Dihydrometanicotine. Metanicotine[4] [8·2 g.; b. p. 154—156°/17 mm.; picrate, m. p. 163—165° (lit., 163°)] was hydrogenated in ethanol (60 c.c.) containing concentrated hydrochloric acid (7 c.c.) over Adams platinum catalyst. After the uptake of hydrogen had ceased, the catalyst was separated and the solvent removed. The residue was made strongly alkaline by excess of sodium hydroxide solution, and the aqueous layer saturated with sodium carbonate. The product was extracted with ether: after removal of the solvent, the residual oil was distilled under reduced pressure and the fraction, b. p. 139—144°/14 mm. (6·6 g.), was collected. The picrate had m. p. 161—163° (lit.,[4] 162—163°).

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Department of Chemistry, The University, Nottingham. [*Received, May 5th*, 1958.]

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[4] Löffler and Kober, *Ber.*, 1909, **42**, 3431.

662. *The Stereoisomers of* 2 : 4-*Dimethyl*-1 : 3-*dioxolan.*

By S. A. Barker, E. J. Bourne, R. M. Pinkard, M. Stacey,
and D. H. Whiffen.

Although 2 : 4-dimethyl-1 : 3-dioxolan has been known for many years,[1] it is only recently that the *cis–trans*-isomers have been separated by Lucas and Guthrie.[2] The present note advances arguments for assigning the *cis*-structure to the lower-boiling isomer (I) and the *trans*-structure to the higher-boiling isomer (II). Three lines of argument support this assignment. First, there is analogy of boiling point with the 1 : 3-dimethyl*cyclo*pentanes. Birch and Dean [3] obtained optically active forms of the higher-boiling 1 : 3-dimethyl*cyclo*pentane which must therefore be the *trans*-isomer. Secondly, and more reliably, by analogy of density with the 1 : 3-dimethyl*cyclo*pentanes: the *cyclo*pentane and the 1 : 3-dioxolan ring are of similar size and shape; at 25°, *trans*-1 : 3-dimethyl*cyclo*pentane is 0·0041 g./c.c. heavier than the *cis*-isomer, whereas the higher-boiling 2 : 4-dimethyl-1 : 3-dioxolan (II) is [2] 0·0065 g./c.c. heavier than isomer (I). Thirdly, Haresnape [4] has given reasons based on strain energies why the *cis*-isomer of 1 : 3-dimethyl*cyclo*pentane should be the more stable. Application of the same arguments to the 2 : 4-dimethyl-1 : 3-dioxolans indicate that the *cis*-isomer would again be the more stable. Equilibrium between the two isomers is readily established in acid conditions and analysis of this mixture by gas-phase chromatography showed it to contain *ca.* 65% of isomer (I) and *ca.* 35% of isomer (II), whether the starting material was pure (I) or pure (II). Hence it is concluded that isomer (I), b. p. 89·7°/742 mm., n_{D}^{19} 1·3950, is the *cis*-isomer, and that (II), b. p. 93·5°/748 mm., $n_{\mathrm{D}}^{19\ 8}$ 1·3963, is the *trans*-isomer.

Experimental.—The mixture of isomers was prepared by a method similar to that of Lucas and Guthrie,[2] namely, exchange reaction between acetaldehyde di-*n*-pentyl acetal and propylene glycol. The isomers were separated by fractional distillation which was repeated until pure fractions were obtained. The fractions were analysed on a gas–liquid partition chromatography column packed with dinonyl phthalate on kieselguhr,[5] nitrogen being used as carrier. The equilibrium studies were made by passing dry hydrogen chloride into each of the pure isomers, refluxing them for 5 hr. at 100°, cooling, neutralising them with silver carbonate, and analysing the products on the chromatography column without further distillation. The quantitative analysis was by comparison with synthetic mixtures.

One of us (R. M. P.) thanks the University of Birmingham for the award of a Fenwick Scholarship.

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[*Received, May* 14*th*, 1958.]

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[1] Gramont, *Bull. Soc. chim. France*, 1884, **41**, 361.
[2] Lucas and Guthrie, *J. Amer. Chem. Soc.*, 1950, **72**, 5490.
[3] Birch and Dean, *J.*, 1953, 2477.
[4] Haresnape, *Chem. and Ind.*, 1953, 1091.
[5] Evans and Tatlow, *J.*, 1955, 1184.