

538. Some Chromium(III) Diamine Phosphates and Arsenates.

By C. V. Y. CHONG, J. P. REDFERN, and J. E. SALMON.

IN the course of our studies on the behaviour of chromium(III) compounds towards heat,¹ we attempted to prepare various trisethylenediamine- and trispropylenediamine-chromium(III) phosphates and arsenates and to study their thermal decomposition by means of a thermobalance.

Experimental.—Addition of either ammonium or sodium phosphates or arsenates (primary, secondary, or tertiary) in 100% excess to solutions of trisethylenediaminechromium(III) sulphate or iodide, followed by cooling of the mixture and, in some cases, addition of alcohol, yielded orange-yellow products containing either sodium or ammonium salts as impurities, which could not be removed by recrystallisation.

Addition of phosphoric acid to concentrated solutions of trisethylenediaminechromium(III) sulphate (analogous to the preparation of the corresponding chloride²) yielded orange-yellow crystals {Found: Cr, 9.7; PO₄, 35.2. [Cr(en)₃]HPO₄·H₂PO₄·6H₂O requires Cr, 9.75; PO₄, 35.6%}. With arsenic acid, in place of phosphoric acid, an intractable gummy product was obtained and attempts to prepare trispropylenediaminechromium(III) phosphates and arsenates by a similar reaction resulted in the formation of brown oils.

A more useful method was one in which a suitable solution of trisethylenediamine- or trispropylenediamine-chromium(III) halide or thiocyanate was shaken for about 3 hr. with solid silver phosphate (or arsenate). The filtrate was cooled and alcohol or acetone added. The various products thus obtained are given in Table I.

TABLE I.
Preparation of some trisdiamine phosphates and arsenates.

Compound	Reactant 1	Reactant 2	Product	Analytical data (%)			
				Cr	N	P or As	Total wt. loss*
(I) [Cr(en) ₃]PO ₄ ·3H ₂ O	[Cr(en) ₃]Cl ₃ (13 g. in 75 ml. of H ₂ O)	AgPO ₄ (15 g.)	Orange- yellow crystals (10 g.)	Found: 13.6 Reqd.: 13.65	21.3 21.6	7.6 7.95	61.3 61.4
(II) [Cr(en) ₃] ₂ (HPO ₄) ₃ ·9H ₂ O	[Cr(en) ₃]Cl ₃ (13 g. in 75 ml. of H ₂ O)	AgPO ₄ (15 g.) and H ₂ PO ₄ (few drops)	Orange- yellow crystals (9 g.)	Found: 11.3 Reqd.: 11.4	18.4 18.4	10.0 10.2	68.0 67.6
(III) [Cr(en) ₃]AsO ₄ ·3H ₂ O	[Cr(en) ₃]Cl ₃ (13 g. in 75 ml. of H ₂ O)	AgAsO ₄ (17 g.)	Fine orange- yellow crystals (12 g.)	Found: 12.05 Reqd.: 12.2	19.6 19.8	17.9 17.7	82.4 82.1
(IV) [Cr(pn) ₃]PO ₄ ·9H ₂ O	[Cr(pn) ₃]Br ₃ (10 g. in 75 ml. of H ₂ O)	AgPO ₄ (11 g.)	Orange- yellow crystals (6 g.)	Found: 9.7 Reqd.: 9.8	16.1 15.8	5.8 5.8	72.5 72.3
(V) [Cr(pn) ₃] ₂ (HAsO ₄) ₃ ·9H ₂ O	[Cr(pn) ₃]Br ₃ (7 g. in 50 ml. of H ₂ O)	AgAsO ₄ (7 g.) and H ₃ AsO ₄ (few drops)	Dark orange- yellow solid †	Found: 9.2 Reqd.: 9.2	15.0 14.9	19.9 19.9	86.6 86.5

* End product on heating to 1200°. For Compounds I, II and IV this was shown to be CrPO₄ and for III and V Cr₂O₃. † Yield uncertain—initial product was an oil.

Analytical methods. The following procedures were used to determine both starting materials and products: (1) chromium, pyrolysis of compound to Cr₂O₃ or CrPO₄; (2) sulphate, gravimetrically as barium sulphate after removal of chromium; (3) chloride, bromide, or iodide, gravimetrically as the silver salt; (4) phosphorus, gravimetrically as ammonium phosphomolybdate after removal of the chromium(III) cation on the strong acid cation exchanger, Zeo-Karb 225 (H⁺ form), (5) arsenic, after reduction, volumetrically with potassium

¹ Lukaszewski and Redfern, *J.*, 1963, 3790.

² Rollinson and Bailar, *Inorg. Synth.*, 1946, 11, 196.

bromate, with α -naphthoflavone as indicator—previous removal of the chromium(III) cation was again necessary; (6) nitrogen, as ammonia, microanalytically by the Alfred Bernhardt Laboratories.

Thermogravimetric studies. All compounds were freshly prepared and vacuum dried. The technique, with a Stanton Thermobalance (model HT-D), has been described before.³ Pre-fired recrystallised alumina crucibles were used in the present studies. Reference runs were carried out in the same crucible and the appropriate corrections were applied throughout. The results are given for sample weights of around 100 mg. from 12-hr. programmes (*i.e.*, $\sim 2^\circ$ min.⁻¹ rise), a chart speed of 12 in./hr. being used. The results are given in Table 2.

TABLE 2.

Thermal decomposition of some trisdiamine phosphates and arsenates.

Compound	(I)	(II)	(III)	(IV)	(V)
Temp. to which hydrate is stable ($^\circ\text{C}$) ...	40 $^\circ$	50	50	35	40
Range of stability of anhydrous compound ($^\circ\text{C}$)	120—150 $^\circ$	210	90—120	155	—
Minimum in dw/dt versus T curve corresponding to loss of 1 diamine molecule ($^\circ\text{C}$)	270 $^\circ$	—	285	260	—
% wt. loss	30.1	—	31.2	43.4	—
Calc. for loss of 1 diamine molecule	29.9	—	26.8	44.4 (+9H ₂ O)	—
Final plateau ($^\circ\text{C}$)	835 $^\circ$	1205	1150	530	1305
Final product	CrPO ₄	CrPO ₄	Cr ₂ O ₃	CrPO ₄	Cr ₂ O ₃

The tertiary phosphates and arsenates (compounds I, III, and IV) show a similar behaviour, in that they lose 1 molecule of diamine at a distinct stage in the decomposition, to trisethylenediamine- and trispropylenediamine-chromium(III) chloride and thiocyanate, as studied by Wendlandt.⁴

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³ Lukaszewski and Redfern, *J.*, 1962, 4802.

⁴ Bear and Wendlandt, *J. Inorg. Nuclear Chem.*, 1961, 17, 286.

539. *Synthesis of [1-¹⁴C]Erythritol and [1-¹⁴C]Threitol.*

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INTEREST in the role of erythritol as a growth factor^{1,2} for *Brucella spp.* and in the activity of substituted threitols as antimetabolites³ led us to explore a route for the synthesis of the [1-¹⁴C]tetritols. Earlier results^{4,5} on the reduction of substituted carboxylic esters by borohydrides suggested that such a synthesis might be achieved⁶ by addition of [¹⁴C]cyanide to glyceraldehyde followed by reduction of the labelled tetrone esters.

DL-Glyceraldehyde (dimer) reacted⁷⁻⁹ readily with potassium [¹⁴C]cyanide in potassium carbonate solution at room temperature to give the mixed epimeric nitriles which were hydrolysed *in situ* to DL-[1-¹⁴C]-erythronic and -threonic acids. After esterification in methanolic hydrogen chloride, the products were reduced⁴ by potassium borohydride in boiling ethanol. Two crystalline products resulted, the major being DL-[1-¹⁴C]erythritol in 33% yield by weight and 28% radioactive yield and the minor product DL-[1-¹⁴C]-threitol.

Since these compounds are derived directly from glyceraldehyde, they would seem to be properly designated with the radioactive atom at C-1. D-[1-¹⁴C]Erythritol has been

¹ Smith, Williams, Pearce, Keppie, Harris-Smith, Fitzgeorge, and Witt, *Nature*, 1962, 193, 47.

² Williams, Keppie, and Smith, *Brit. J. Exp. Path.*, 1962, 43, 530.

³ Smith, Kent, and Timmis, *Brit. Prov. Pat.* 366/62.

⁴ Barnett and Kent, *J.*, 1963, 2743.

⁵ Kent, Welch, and Wood, *J.*, 1964, 2493.

⁶ Isbell, Karabinos, Frush, Holt, Schwebel, and Galkowski, *J. Res. Nat. Bur. Stand.*, 1952, 48, 163.

⁷ Kiliani, *Ber.*, 1886, 19, 3029; 1887, 20, 282, 339.

⁸ Fischer, *Ber.*, 1889, 22, 2204.

⁹ Miltzer, *Arch. Biochem.*, 1946, 9, 91.

described¹⁰ in chromatographic amounts as the product of catalytic reduction of L-[4-¹⁴C]-erythrulose. A chemical synthesis of the individual isomers may be expected *via* the above route from the appropriate starting material.

Experimental.—[1-¹⁴C]tetronic acids. A solution of radioactive potassium cyanide (0.144 g., 2.21 mmoles; 0.5 mc.; Radiochemicals Ltd., Amersham) and potassium hydroxide (0.14 g., 2.5 mmoles) in water (5 ml.) was frozen at -78° . To this solid carbon dioxide (1.2 g.) was added together with an aqueous solution of DL-glyceraldehyde (20 ml.; 0.20 g., 2.22 mmoles; Light & Co., Colnbrook) and the mixture allowed to warm up slowly to room temperature in a stoppered vessel.

After 12 hr. at 4° and 2 days at room temperature the addition product was hydrolysed by raising the temperature to 50° for 4 hr. and then to 95° for 1 hr.

Cations were removed by stirring the solution with excess of Amberlite IR120 resin (H⁺, analytical grade) for 1 hr. Centrifugation and removal of solvent (at 14 mm.) left a pale yellow syrup, excess of hydrogen [¹⁴C]cyanide being collected during concentration in a potassium hydroxide trap.

Methyl [1-¹⁴C]tetronates. The resulting mixture of isomeric acids was dissolved in methanolic hydrogen chloride (*ca.* 10 ml.; 1.5% w/w) and refluxed gently for 20 hr. The solution was neutralised while still warm (basic lead carbonate), filtered, and evaporated to dryness at 14 mm., giving the mixed esters as a pale yellow syrup (0.27 g.).

DL-[1-¹⁴C]erythritol. A suspension of potassium borohydride (0.3 g., 5.6 mmoles) in ethanol (25 ml.) at room temperature was added to a magnetically-stirred solution of the methyl esters (0.27 g.) in dry ethanol (30 ml.). The temperature was then raised to 70° for 8 hr., and methanolic hydrogen chloride (10 ml.; 10% w/w) together with methanol (50 ml.) added to the cooled solution. Methanol, ethanol, and methyl borate were distilled off until the distillate no longer gave a green flame; the residue was then neutralised (basic lead carbonate), filtered, and evaporated under reduced pressure.

The residual syrup was dissolved in water (10 ml.) and stirred for 1 hr. with Dowex 1 and with Amberlite IR 120 (to remove salts). Freeze-drying of the filtered solution gave a partially crystalline clear syrup which was mixed with a few drops of hot ethanol. After 22 hr. at -5° a mass of white crystals was obtained, which after recrystallisation from ethanol gave DL-[1-¹⁴C]-erythritol, m. p. 120° (89 mg.; 0.14 mc., 33%; radiochemical yield 28%; lit.,¹¹ m. p. 121°). Chromatography (Whatman No. 1, butanol-ethanol-water: 4:1:5) gave a single spot (R_F 0.28), detected by sodium periodate followed by benzidine in methanol¹² and by radioactive scanning, moving identically with erythritol.

Concentration of the mother-liquors gave DL-[1-¹⁴C]threitol which after recrystallisation from ethanol had m. p. 72° (lit.,¹³ m. p. 72°).

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¹⁰ Batt, Dickens, and Williamson, *Biochem. J.*, 1960, **77**, 272.

¹¹ Lespieau, *Compt. rend.*, 1907, **144**, 145.

¹² Cifonelli and Smith, *Analyt. Chem.*, 1954, **26**, 1132.

¹³ Griner, *Compt. rend.*, 1893, **117**, 553.

540. Preparation of Some N-Substituted Halogeno-anilines and -anilides by an Improved N-Alkylation.

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SOME hitherto unknown N-alkylanilines have been readily prepared from anilines, using alkyl halides and lithium amide, by a modification of a procedure previously used for tertiary heterocyclic amines.¹ The preparation of *p*-chloro-N-(4-chlorobenzyl)aniline by the reductive alkylation of *p*-chloroaniline with *p*-chlorobenzaldehyde in the presence of formic acid was also investigated. In contrast with the results obtained with heterocyclic amines,² the product isolated (in high yield) was the N-formyl-derivative of the

¹ Kaye and Kogon, *J. Amer. Chem. Soc.*, 1951, **73**, 5891.

² Kaye and Kogon, *Rec. Trav. chim.*, 1952, **71**, 309.

TABLE I.
N-Alkylanilines.

Product	Method	Yield (%)	B. p./mm. or m. p.	n_D (temp.)	Formula	Found (%)			Reqd. (%)		
						C	H	N	C	H	N
1. 4-Cl·C ₆ H ₄ ·NH ₂ ·[CH ₂] ₂ ·Me	A	77	146—148°/20	1.5543 (26)	C ₉ H ₁₃ ClN	63.7	7.0	63.7	63.7	7.0	63.7
2. 4-Cl·C ₆ H ₄ ·NH ₂ ·[CH ₂] ₃ ·Me	A	86	161—163/20	1.5462 (25)	C ₁₀ H ₁₅ ClN	65.3	7.6	65.4	65.4	7.7	65.4
3. 4-Cl·C ₆ H ₄ ·NH ₂ ·[CH ₂] ₄ ·Me	A	88	167—168/17	1.5400 (25)	C ₁₁ H ₁₆ ClN	66.7	7.9	66.8	66.8	8.2	66.8
4. 4-Cl·C ₆ H ₄ ·NH ₂ ·[CH ₂] ₅ ·CHMe ₂	A	89	159—159.5/16	1.5382 (25)	C ₁₁ H ₁₆ ClN	67.0	8.1	66.8	66.8	8.2	66.8
	B	79	203—204 (vac.) (HBr, from propan-2-ol)	—	C ₁₁ H ₁₅ BrClN	47.3	6.2	47.4	47.4	6.2	47.4
	A	89	187—188.5 (vac.) (HCl, from propan-2-ol)	—	C ₁₁ H ₁₅ ClN	56.3	7.5	56.4	56.4	7.3	56.4
5. 4-Cl·C ₆ H ₄ ·NH ₂ ·[CH ₂] ₇ ·Me	A	89	124—125/0.1	1.5222 (30)	C ₁₄ H ₂₂ ClN	70.2	9.5	70.1	70.1	9.3	70.1
	A	85	30.1—30.4 (free base)	—	—	—	—	—	—	—	—
6. 4-Cl·C ₆ H ₄ ·NH ₂ ·[CH ₂] ₁₁ ·Me	A	85	49.0—49.6 (free base, from methanol)	—	C ₁₆ H ₂₄ Cl ₂ N ₂ H ₂ O	63.0	9.4	63.3	63.3	9.5	63.3
	A	78	113—115 (hydrochloride, from acetone)	—	C ₁₃ H ₁₈ Cl ₂ N ₂ HCl	54.5	4.2	54.1	54.1	4.2	54.1
7. 4-Cl·C ₆ H ₄ ·NH ₂ ·CH ₂ ·C ₃ H ₇ ·Cl-4	A	78	71.0—71.2 (free base, from hexane; lit., ⁵ 65—66°)	—	—	—	—	—	—	—	—
8. 4-Br·C ₆ H ₄ ·NH ₂ ·CH ₂ ·C ₆ H ₄ ·Cl-4	B	77	189.5—190 (vac.) (HCl, from propan-2-ol)	—	C ₁₃ H ₁₂ BrCl ₂ N	47.0	3.8	46.9	46.9	3.6	46.9
9. 4-Cl ₂ ·C ₆ H ₃ ·NH ₂ ·CH ₂ ·C ₃ H ₇ ·Cl-4	A	80	55.0—55.5 (free base, from heptane)	—	C ₁₃ H ₁₆ Cl ₂ N	54.3	3.8	54.5	54.5	3.5	54.5
	D	95	190—190.5 (vac.) (HCl, from propan-2-ol)	—	C ₁₃ H ₁₁ Cl ₂ N	48.5	3.3	48.3	48.3	3.4	48.3

TABLE 2.
N-Acyl-N-alkylanilines.

Amide	Yield (%)	B. p./mm. or m. p.	n_D (temp.)	Formula	Found (%)			Required (%)		
					C	H	N	C	H	N
(3) -CO·CH ₂ ·Cl	99*	133—134/0.1	1.5372 (25)	C ₁₃ H ₁₇ Cl ₂ NO	57.1	6.3	—	56.9	6.3	—
(3) -CO·CH ₂ ·SCN	100	—	1.5508 (25)	C ₁₄ H ₁₇ ClN ₂ OS	—	—	—	—	—	—
(4) -CHO	95	119/0.15	1.5361 (20)	C ₁₃ H ₁₆ ClNO	64.2	7.0	—	63.9	7.2	—
(4) -COMe	97	112/0.2	1.5236 (19)	C ₁₃ H ₁₆ ClNO	65.2	7.2	—	65.1	7.6	—
(4) -CO·CH ₂ ·Cl	98*	126—127/0.1	1.5370 (25)	C ₁₃ H ₁₇ Cl ₂ NO	57.1	6.3	—	56.9	6.3	—
(4) -CO·CH ₂ ·SCN	98	—	1.5496 (25)	C ₁₄ H ₁₇ Cl ₂ OS	—	—	—	—	—	—
(5) -CHO	98	160/0.1	1.5236 (20)	C ₁₆ H ₂₂ ClNO	67.4	8.4	—	67.3	8.3	—
(5) -COMe	95	150/0.1	1.5141 (19)	C ₁₆ H ₂₄ ClNO	68.4	8.8	—	68.2	8.6	—
(5) -CO·CH ₂ ·Cl	95*	170—174/0.1	1.5239 (25)	C ₁₆ H ₂₂ Cl ₂ NO	61.1	7.4	—	60.8	7.3	—
(5) -CO·CH ₂ ·SCN	100	—	1.5390 (25)	C ₁₇ H ₂₃ Cl ₂ OS	—	—	—	—	—	—
(6) -CO·CH ₂ ·Cl	96*	23.4 (f.p.)	—	C ₂₀ H ₃₁ Cl ₂ NO	—	—	—	—	—	—
(6) -CO·CH ₂ ·SCN	99	31.8 (f.p.)	—	C ₂₁ H ₃₃ Cl ₂ NO	—	—	—	—	—	—
(7) -COMe	92	106—106.5 (from CCl ₄)	—	C ₁₆ H ₂₂ Cl ₂ NO	—	—	—	—	—	—
(7) -CO·CH ₂ ·Cl	92†	101.7—102.4 (vac.) †	—	C ₁₅ H ₁₈ Cl ₂ NO	61.0	4.3	—	61.2	4.5	—
(7) -CO·CH ₂ ·SCN	93	99.5—100.5 †	—	C ₁₅ H ₁₈ Cl ₂ NO	54.6	3.7	—	54.8	3.7	—
(8) -CO·CH ₂ ·Cl	93†	102.2—102.7 (from heptane)	—	C ₁₆ H ₂₂ Cl ₂ N ₂ OS	54.9	3.8	—	54.7	3.5	—
(8) -CO·CH ₂ ·SCN	99	104.8—105.3 †	—	C ₁₆ H ₁₂ BrCl ₂ NO	48.0	3.3	—	48.3	3.2	—
(9) -CO·CH ₂ ·Cl	92†	75.7—76.4 †	—	C ₁₈ H ₂₂ BrCl ₂ NO	48.5	3.0	—	48.6	3.1	—
(9) -CO·CH ₂ ·SCN	100	126.6—127.3 §	—	C ₁₅ H ₁₁ Cl ₂ NO	49.5	3.1	—	49.6	3.1	—
				C ₁₆ H ₁₁ Cl ₃ N ₂ OS	49.9	2.8	—	49.8	2.9	—

* Method C. † Method D. ‡ From di-isopropyl ether. § From methanol. Crude product initially had m. p. 73.6—74.6°; after standing at room temperature for 1 month it had m. p. 125.4—126.7°. ¶ Chlorine analysis.

expected secondary amine. A good yield of the latter could be obtained readily by hydrolysis without isolation of the intermediates. The *N*-substituted anilines are listed in Table 1; most were converted into their α -chloro- and α -thiocyanato-acetanilide derivatives (Table 2).

Experimental.—Melting points are corrected, and were determined in open capillaries, except for those designated "vac.," which were observed in capillaries evacuated to about 0.1 mm.

Lithium amide assay. Yields were significantly higher in the alkylations when equivalent amounts of the reactants were employed. Since lithium amide deteriorated slowly, even when stored in a tightly-stoppered screw-cap bottle sealed with paraffin wax, the following method for determining its exact titre was devised.

A small vial, containing lithium amide (40—70 mg.; Lithium Corp. of America), was placed in a 500-ml. Kjeldahl flask which was then connected by a Hopkins distillation head to a condenser, set for downward distillation, whose end was immersed in 2% boric acid solution (10 ml.) containing several drops of a Methyl Red–Bromocresol Green indicator.³ Almost immediately 3% aqueous sodium hydroxide was added to the sample from a tap-funnel, and the solution was distilled. After 80—90 ml. of distillate had been collected, the receiver was lowered so that the end of the condenser was above the surface of the distillate; a total of 110 ml. was collected. The ammonia content was determined by titration with 0.1*N*-acid, a blank run also being done.

In most preparations lithium amide of 82.8% purity was employed, though no difference in yield was apparent when the purity was 78—91%. A sample stored in a tightly-stoppered bottle in a desiccator over potassium hydroxide showed no change in the titre after 4 months.

p-Chloro-*N*-*n*-pentylaniline (Method A). The following procedure was used in the preparation of all but one of the *N*-substituted alkylanilines in Table 1. A mixture of *p*-chloroaniline (63.8 g.; redistilled b. p. 116°/19 mm.) and toluene (200 ml.) was dried by distillation (50 ml. of distillate collected). After the solution had cooled to room temperature, *n*-pentyl bromide (75.5 g.) and lithium amide (14.2 g.; 81.2%) were added, and the mixture was heated to reflux. The exothermic reaction which occurred at this point moderated on removal of the source of heat, and was accompanied by the evolution of ammonia and precipitation of lithium bromide. The reactants were heated under reflux for 16 hr.; stirring did not improve the yield. When cooled to room temperature, the mixture was diluted with benzene, toluene, or hexane (100 ml.), filtered through a layer of a diatomaceous earth, and the filtrate distilled *in vacuo*. After removal of the solvent, a forerun (8.5 g.), b. p. 131—154°/16 mm., was dissolved in hexane (*ca.* 30 ml.), chilled in an ice-bath, seeded, and left at 0° for a few hours. Filtration gave *p*-chloroaniline (1.26 g.; 2.0%). The filtrate was combined with the residue in the distillation flask and distilled, to give the colourless product, b. p. 82.5—87°/0.007—0.015 mm. (86.4 g.; 88%); it was redistilled for analysis. The oxalic acid salt, precipitated (76%) on treating the secondary amine with an excess of oxalic acid in propan-2-ol, had m. p. 150.5—152.5°⁴ after two recrystallisations from this solvent. Further recrystallisation lowered the m. p.

When the reaction was carried out on a larger scale, and especially when the more reactive 4-chlorobenzyl chloride was used, the initial exothermic reaction could be controlled by adding the halide, as rapidly as possible, to a mixture of the aniline, lithium amide, and toluene, while stirring and heating the mixture under reflux. In these preparations 1.0—4.0% (usually 1—2%) of the starting amine was recovered. The recovery is not limited to *p*-chloroaniline alone, for, in the preparation of 3,4-dichloro-*N*(4-chlorobenzyl)aniline, 3,4-dichloroaniline (5.73 g.; 4.0%), m. p. 71—72.5°, was obtained. The reported yields (including those in Table 1) are not corrected for the amounts of halogenoaniline recovered.

p-Chloro-*N*-isopentylaniline hydrobromide (Method B). The preparation of this salt, from *p*-chloroaniline (12.8 g.), lithium amide (2.84 g.; 81.2%), isopentyl bromide (15.1 g.), and toluene (40 ml.), differed from method A only in the isolation of the product. A mixture of benzene and propan-2-ol (100 ml.; 1 : 1) was added dropwise to the mixture after refluxing; ammonia was liberated copiously during this addition. Hydrobromic acid (25 ml.; 48%) was added, the mixture was dried by heating it under reflux and collecting an aqueous phase in a water-trap, and most of the solvent was removed at 95° in a current of air. The residue was dissolved

³ Ma and Zuazaga, *Ind. Eng. Chem. Analyt.*, 1952, **14**, 280.

⁴ Elderfield and Green, *J. Org. Chem.*, 1952, **17**, 431.

in hot propan-2-ol (200 ml.) and 150 ml. of the solvent was distilled off. After chilling in an ice-bath, the white flakes of the hydrobromide were filtered off, washed with cold propan-2-ol, and dried at 95° (221 g.; 79%).

This procedure required modification for the preparation of *p*-bromo-*N*-(4-chlorobenzyl)-aniline hydrochloride. Since ammonium chloride is insoluble in the lower alcohols, it was necessary to filter the mixture at the end of the reaction, and concentrate the filtrate. Otherwise the isolation was identical with the preceding, except that concentrated hydrochloric acid (100 ml. per 0.5 mole of *p*-chloroaniline) was used in place of hydrobromic acid.

p-Chloro-*N*-(4-chlorobenzyl)formanilide. A mixture of *p*-chloroaniline (63.8 g.), *p*-chlorobenzaldehyde (77.3 g.), and benzene (175 ml.; dried over calcium hydride) was heated under reflux until water was no longer collected in a water-trap. [*p*-Chloro-*N*-(4-chlorobenzylidene)-aniline, could be obtained in 95% yield, m. p. 109—110.5°,⁵ on chilling a reaction mixture which contained heptane (200 ml.) in place of the benzene.] After removal of the solvent by distillation, formic acid (27 ml.; 88%) was added and the solution heated under reflux (20 hr.; after 7 hr. carbon dioxide was no longer liberated). Cumene was added and the upper colourless aqueous formic acid layer was removed by azeotropic distillation. The cumene was removed *in vacuo* and the formanilide, a viscous yellow oil, was collected at 156°/0.01 mm. (131.8 g.; 94%), m. p. 72.5—73.5° (from methanol) (Found: C, 59.9; H, 4.0. C₁₄H₁₁Cl₂NO requires C, 60.2; H, 4.0%).

p-Chloro-*N*-(4-chlorobenzyl)aniline hydrochloride. The formanilide was hydrolysed *in situ* by adding propan-2-ol (150 ml.) and concentrated hydrochloric acid (50 ml.) to the mixture at the end of the reflux period (20 hr.). Refluxing was continued for 2—3 min. after the acid had been added; at this point the product began to precipitate and a vigorous exothermic reaction ensued. External heating was discontinued and the mixture cooled to 0° after spontaneous ebullition had ceased. The white powder was filtered off and washed well with ice-cold propan-2-ol and ether (69.5 g.; 80%), m. p. 198—200° (from propan-2-ol).

Acylated N-alkylanilines. *p*-Chloroformanilides were prepared by heating under reflux a mixture of the amine (0.1 mole), formic acid (23 ml.; 90%), and toluene (20 ml.) until no more water collected in a water-trap, and the exothermic reaction had ceased. The products were collected by distillation. Acetamides were obtained by heating with acetic anhydride at 100°. Chloroacetamides were prepared either by the method of Speziale and Hamm⁶ (method C) or by heating the secondary amine (2 moles) with chloroacetyl chloride (1 mole) in benzene (method D). In the latter procedure the excess of amine was recovered almost quantitatively as its hydrochloride. Thiocyanatoacetamides were synthesised by heating the chloroacetamides (0.2 mole) with sodium thiocyanate (0.24 mole) in acetone (100 ml.). The *N*-4-chlorobenzylthiocyanato-derivatives were recrystallised, but the *N*-alkyl derivatives were liquids at room temperature and decomposed on attempted distillation at low pressures; they were all obtained in quantitative yield, and were 94.8—98.6% pure (by analysis).

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⁵ Roe and Montgomery, *J. Amer. Chem. Soc.*, 1953, **75**, 910.

⁶ Speziale and Hamm, *J. Amer. Chem. Soc.*, 1956, **78**, 2556.

541. *o*-Hydroxycarbonyl Compounds.

By I. A. KAYE, R. S. MATTHEWS, and A. A. SCALA.

THE preparations of the *peri*-oriented β-diketones, hexahydroindane-1,7- and decalin-1,8-dione, were recently described.¹ These compounds hold promise as chelating agents of greater selectivity than their flexible analogues since each exists almost entirely as a *cis*-enol in which the distance between the functional groups is fixed by the geometry of the molecule. Since the *peri*-hydroxycarbonyl compounds,² 7-hydroxy-1-indanone and 8-hydroxy-1-tetralone, have the same potential, derivatives of these complexing agents,

¹ Kaye and Matthews, *J. Org. Chem.*, 1963, **28**, 325.

² Hayes and Thomson, *J.*, 1956, 1585.

containing nitro-groups *ortho* and/or *para* to their hydroxyl groups, have also been synthesised. The preparation of these hitherto unknown products, their methyl ethers, and some related compounds are described.

The mixture of mononitro-derivatives, obtained on nitrating each of the *peri*-hydroxycarbonyl compounds in acetic acid with nitric acid,³ was separated by chromatography. 8-Hydroxy-5-nitro-1-tetralone was identified by converting it into the known 5,8-dihydroxy-1-tetralone.⁴ A distinction between the mononitro-7-hydroxy-1-indanones was effected by comparing their absorption bands in the 297—350 m μ region with those of 3- and 5-nitro-salicylaldehyde and -acetophenone and 8-hydroxy-5- and -7-nitro-1-tetralone (cf. Table). The product absorbing at the longer wavelength is assigned the 7-hydroxy-6-nitro-1-indanone structure since the other carbonyl compounds possessing an *o*-nitrophenol moiety also absorbed at longer wavelength than their *para*-isomers. The structural assignments are supported by the fact that each of the mononitro-7-hydroxy-1-indanones parallels its tetralone analogue in ease of elution from a column of alumina and in reduction at a dropping-mercury electrode.⁵

Ultraviolet absorption spectra (λ in m μ ., log ϵ in parentheses).

Compound	$\lambda_{\max.}$	$\lambda_{\min.}$	$\lambda_{\max.}$
5-Nitrosalicylaldehyde	230 (3.92)	258 (3.32)	310 (4.00)
3-Nitrosalicylaldehyde	278 (3.82)	311 (3.32)	350 (3.57)
2-Hydroxy-5-nitroacetophenone	235 (4.24)	264 (3.53)	302 (4.03)
2-Hydroxy-3-nitroacetophenone	238 (4.23)	289 (3.13)	335 (3.79)
8-Hydroxy-5-nitro-1-tetralone	249 (4.20)	274 (3.67)	297—298 (3.80)
8-Hydroxy-7-nitro-1-tetralone	245 (4.35)	296 (3.25)	342 (3.90)
7-Hydroxy-4-nitro-1-indanone	232 (4.16)	273 (3.63)	319 (3.87)
7-Hydroxy-6-nitro-1-indanone	242 (4.13)	304—305 (3.30)	334 (3.53)

The ability of acetyl nitrate to dinitrate 7-hydroxy-1-indanone and 8-hydroxy-1-tetralone represents a novel application of this reagent.⁶ When applied to 2-hydroxyacetophenone, however, the only product recovered was picric acid; with salicylaldehyde a tarry product was formed. Physical properties of several of these *o*-hydroxycarbonyl compounds have been investigated.⁷

Experimental.—Unless otherwise indicated, m. p.s are corrected and ultraviolet spectra were determined in 95% ethanol; in the case of the phenols the solutions were 0.0048N in hydrochloric acid. Infrared values represent strong peaks and were observed in potassium bromide discs. The acid-washed alumina had an activity of I/II.

Naphthalene-1,8-diol, m. p. 140—141° (from ether-hexane), $\lambda_{\max.}$ 227 m μ (log ϵ 4.74), 305 (3.83), 320 (3.88), and 333 (3.90), was obtained (53%) from the sulfone of 1-hydroxynaphthalene-8-sulphonic acid.⁸ 7-Hydroxy-1-indanone, m. p. 109.5—111° (sublimed at 80°/25 mm.), $\lambda_{\max.}$ 256 m μ (log ϵ 4.04) and 314—315 (3.52), $\lambda_{\min.}$ 233 m μ (log ϵ 3.50) and 273 (2.57), was isolated (28%) from a Fries rearrangement of phenyl 2-chloropropionate, using the method described for the preparation of 4-bromo-7-hydroxy-1-indanone.⁹

2-Acetoxy-3-nitrobenzylidene diacetate. The triacetate, prepared by the oxidation of 2-methyl-6-nitrophenyl acetate,¹⁰ following the procedure used for the preparation of 2-nitrobenzylidene diacetate,¹¹ had m. p. 97.2—98.2° (from di-isopropyl ether), significantly below that (110°) reported previously¹⁰ (Found: C, 50.5; H, 4.3; N, 4.5. Calc. for C₁₃H₁₃NO₈: C, 50.2; H, 4.2; N, 4.5%). On hydrolysis,¹¹ 3-nitrosalicylaldehyde, m. p. 108.6—109.3° (needles), was obtained (94%), identical (mixed m. p. and infrared spectrum) with a sample prepared by the nitration of salicylaldehyde in acetic acid with fuming nitric acid.¹² 2-Methoxy-3-nitrobenzaldehyde, prepared (63%) by treating a solution of 3-nitrosalicylaldehyde in ether

³ Joshi and Singh, *J. Amer. Chem. Soc.*, 1954, **76**, 4993.

⁴ Thomson, *J.*, 1952, 1822.

⁵ Peterson, M.A. Thesis, Brooklyn College, 1962.

⁶ Bordwell and Garbisch, *J. Amer. Chem. Soc.*, 1960, **82**, 3588.

⁷ Magnusson, Postmus, and Craig, *J. Amer. Chem. Soc.*, 1963, **85**, 1711.

⁸ Böeseken, *Rec. Trav. chim.*, 1939, **58**, 3.

⁹ Barnes, Kraft, and Gordon, *J. Amer. Chem. Soc.*, 1949, **71**, 3523.

¹⁰ Ichibagase and Terada, *J. Pharm. Soc. Japan*, 1952, **72**, 878.

¹¹ Tsang, Wood, and Johnson, *Org. Synth.*, 1955, Coll. Vol. III, 641.

¹² Gilliland, Hart, and Everett, *Proc. Oklahoma Acad. Sci.*, 1941, **21**, 119 (*Chem. Abs.*, 1942, **36**, 438).

with an excess of diazomethane, had m. p. 97.2—97.7° from propan-2-ol (lit.,¹³ 102°), λ_{\max} 236 μ (log ϵ 4.02) and 304 (3.26), λ_{\min} 222 μ (log ϵ 3.94) and 284 (3.19) (Found: C, 53.1; H, 4.1; N, 7.6. Calc. for $C_9H_7NO_4$: C, 53.0; H, 3.9; N, 7.7%).

2-Methoxy-5-nitrobenzaldehyde dimethyl acetal. *o*-Anisaldehyde (20.0 g.) was added during 1 hr. to a mixture of concentrated nitric (20 ml.) and sulphuric (40 ml.) acids at -5 to -10°. After 1 hr. at +5°, the mixture was poured into cold water (240 ml.). Extraction with ether and crystallisation from methanol gave the *acetal* (12.5 g., 37%), m. p. 67—68° (from propan-2-ol) (Found: C, 52.4; H, 5.7; N, 6.2. $C_{10}H_{13}NO_5$ requires C, 52.9; H, 5.8; N, 6.2%). No carbonyl absorption was evident in its infrared spectrum. On hydrolysis with concentrated hydrochloric acid, 2-methoxy-5-nitrobenzaldehyde was obtained (94%), m. p. 86.5—87° (from propan-2-ol), λ_{\max} 238—239 μ (log ϵ 4.10) and 303—304 (4.04), λ_{\min} 265—266 (3.66), identical (mixed m. p. and infrared spectrum) with a sample obtained by methylating 5-nitrosalicylaldehyde¹² with diazomethane in ether.

2-Methoxy-3-nitroacetophenone. Although 2-methoxy-5-nitroacetophenone,¹⁴ m. p. 96—97° (from ether-hexane), could be obtained in 52% yield by heating the sodium salt of 2-hydroxy-5-nitroacetophenone³ with methyl iodide in ethanol, an attempt to prepare the 3-nitro-isomer by this method was unsuccessful. The latter was synthesised (96%) by treating 2-hydroxy-3-nitroacetophenone³ with diazomethane in ether. It had m. p. 41.8—42.6° (from propan-2-ol) (Found: C, 55.3; H, 4.6; N, 7.2. $C_9H_9NO_4$ requires C, 55.4; H, 4.7; N, 7.2%).

2-Methoxy-3,5-dinitroacetophenone. Prepared (96%) from 2-hydroxy-3,5-dinitroacetophenone³ and diazomethane in ether, the *methyl ether* had m. p. 69.9—71.4° (from propan-2-ol) (Found: C, 44.6; H, 3.2; N, 11.7. $C_9H_8N_2O_6$ requires C, 45.0; H, 3.4; N, 11.7%).

3- and 5-Amino-2-hydroxyacetophenone hydrochlorides. Hydrogenation of 2-hydroxy-5-nitroacetophenone³ (2.0 g.) in methanol (75 ml.) in the presence of platinum oxide (10 mg.) at 25° and atmospheric pressure gave *5-amino-2-hydroxyacetophenone*, isolated as its *hydrochloride* (1.0 g., 49%), decomposing at 247—250° (uncorr.) [from methanol-propan-2-ol (1:1)], λ_{\max} 245 μ (log ϵ 3.59) and 323—324 (3.62), λ_{\min} 230 μ (3.69) and 270 (2.80) (Found: C, 51.3; H, 5.1; N, 7.5. $C_8H_{10}ClNO_2$ requires C, 51.2; H, 5.4; N, 7.5%). The free base showed λ_{\max} 233 μ (log ϵ 4.33) and λ_{\min} 293 (2.81). *3-Amino-2-hydroxyacetophenone hydrochloride*, prepared similarly (1.8 g., 87%), decomposed at 224—227° (uncorr.), λ_{\max} 246 μ (log ϵ 3.97) and 319 (3.53), λ_{\min} 227 (3.64) and 269 (3.21) (Found: C, 51.0; H, 5.4; N, 7.4%). The free base showed λ_{\max} 235—236 μ (log ϵ 4.18) and 275 (3.88), λ_{\min} 259—260 (3.73) and 310 (2.81).

8-Acetoxy-1-tetralone. 8-Hydroxy-1-tetralone, b. p. 81°/0.11 mm., n_D^{20} 1.5871, λ_{\max} 258.5 μ (log ϵ 3.99) and 333 (3.52), was obtained (92.1 g., 95%) by hydrogenating naphthalene-1,8-diol (96.1 g.) in absolute ethanol (100 ml.) in the presence of palladium-charcoal (5.0 g.; 10%) at 60° and 4 atm. The *copper complex*, crystallised from benzene, did not melt below 300°, λ_{\max} 6.25, 6.32, 6.54, 7.02, and 8.09 μ (Found: C, 62.0; H, 5.1; Cu, 16.5. $C_{20}H_{18}CuO_4$ requires C, 62.3; H, 4.7; Cu, 16.5%). The *acetate*, prepared by heating the keto-phenol in acetic anhydride in the presence of phosphoric acid for a few minutes, had m. p. 80.6—81° (from hexane), λ_{\max} 248 μ (log ϵ 3.95), λ_{\max} 5.68 and 5.97 μ (Found: C, 70.3; H, 5.8. $C_{12}H_{12}O_3$ requires C, 70.6; H, 5.9%).

8-Hydroxy-5-nitro-1-tetralone. A mixture of 8-hydroxy-5- and -7-nitro-1-tetralone was obtained by adding concentrated nitric acid (12 ml.) to a solution of 8-hydroxy-1-tetralone (16.2 g.) in glacial acetic acid (56 ml.) at 46—49°. After 1 hr. at this temperature the solution was diluted to ca. 225 ml. The yellow solid (17.5 g.), after filtration, washing with cold water, and air-drying, was dissolved in benzene (250 ml.) and chromatographed on alumina (410 g.). The *5-nitro-isomer* (5.59 g., 27%) was eluted with benzene (2200 ml.), m. p. 97—98° (from hexane), λ_{\max} 6.08, 6.60, and 7.45 μ (Found: C, 57.8; H, 4.7; N, 6.8. $C_{10}H_9NO_4$ requires C, 58.0; H, 4.4; N, 6.8%). The *copper complex*, washed well with hot benzene and ether, did not melt below 300°, λ_{\max} 6.27, 6.47, 6.69, 7.27, and 7.50 μ (Found: C, 50.3; H, 3.5; Cu, 13.2. N, 5.7. $C_{20}H_{16}CuN_2O_8$ requires C, 50.5; H, 3.4; Cu, 13.4; N, 5.9%). *8-Methoxy-5-nitro-1-tetralone*, prepared by heating the sodium salt of the phenol with an excess of methyl iodide in dry ethanol, had m. p. 80.8—81.6° (from ether-hexane), λ_{\max} 242—244 μ (log ϵ 4.12) and 304—305 (3.82), λ_{\max} 5.92 μ (Found: C, 59.6; H, 5.2; N, 6.4. $C_{11}H_{11}NO_4$ requires C, 59.7; H, 5.0; N, 6.3%).

8-Hydroxy-7-nitro-1-tetralone. By elution of the alumina column (from which the bulk of the

¹³ Chakravarti, *Current. Sci.*, 1935, 4, 26.

¹⁴ Mathieson and Newberry, *J.*, 1949, 1133.

5-nitro-isomer had been removed) with additional benzene (400 ml.), a mixture of the 2-mono-nitro-derivatives (0.418 g.) was obtained. The 7-nitro-product (3.08 g., 15%) was then eluted with ether (1 l.) and formed pale yellow needles, m. p. 128—129° (from hexane), λ_{\max} . 6.09, 6.61, and 7.48 μ (Found: C, 57.8; H, 4.7; N, 6.8. $C_{10}H_9NO_4$ requires C, 58.0; H, 4.4; N, 6.8%). The copper complex, λ_{\max} . 6.25br, 6.60, and 7.46 μ , did not melt below 300° (Found: C, 50.2; H, 3.7; Cu, 13.5; N, 5.9%). An attempt to prepare the methyl ether by the action of methyl iodide on the sodium salt of the phenol failed. 8-Methoxy-7-nitro-1-tetralone, m. p. 85.2—86.5° (from methanol), λ_{\max} . 240—241 m μ (log ϵ 4.25) and 302 (3.52), λ_{\min} . 224 (4.12) and 291 (3.51), was prepared in low yield by treating a solution of the phenol in tetrahydrofuran with diazomethane (Found: C, 59.4; H, 5.1%).

8-Hydroxy-5,7-dinitro-1-tetralone. A solution of 8-hydroxy-1-tetralone (4.0 g.) in acetic anhydride (30 ml.) was added to a stirred solution of sulphuric acid (0.6 ml.) in acetic anhydride (220 ml.) at -5 to -10°. After 1 hr. at -5, the solution was diluted with ice (1600 ml.) and sodium hydrogen carbonate (90.0 g.) was added. The crude water-washed and air-dried product (4.08 g., 66%) had m. p. 96.3—96.9° (from methanol), λ_{\max} . 241—242 m μ (log ϵ 4.33) and 336 (3.75), λ_{\min} . 6.01 μ (Found: C, 47.6; H, 3.2; N, 11.0. $C_{10}H_8N_2O_6$ requires C, 47.6; H, 3.2; N, 11.1%). 8-Hydroxy-5,7-dinitro-1-tetralone could also be obtained by nitrating either the 8-hydroxy-5- or -7-nitro-1-tetralone by the same procedure. Under the same conditions, but in the absence of nitric acid, 8-hydroxy-1-tetralone and its mononitro-derivatives were acetylated. This inability to prepare an acetate of the dinitro-compound is not without precedent.^{15,16} The green copper complex, recrystallised from acetone-propan-2-ol, did not melt below 300°, λ_{\max} . 6.19, 6.40, 6.55, and 7.48 μ (Found: C, 42.4; H, 2.7; Cu, 11.2; N, 10.0. $C_{20}H_{14}CuN_4O_{12}$ requires C, 42.5; H, 2.5; Cu, 11.2; N, 9.9%).

5- and 7-Amino-8-hydroxy-1-tetralone. These were prepared as for the aminohydroxy-acetophenones and were isolated as their free bases (93%). 5-Amino-8-hydroxy-1-tetralone had m. p. 135—136 (from di-isopropyl ether), λ_{\max} . (in EtOH) 240 m μ (log ϵ 4.22) and 390.5 (3.51), λ_{\min} . (in EtOH) 297 (2.44), λ_{\max} . 3.00, 3.09, and 6.14 μ (Found: C, 67.6; H, 6.4; N, 7.9. $C_{10}H_{11}NO_2$ requires C, 66.8; H, 6.3; N, 7.9%). The hydrochloride, after recrystallisation from propan-2-ol, did not melt below 325°, λ_{\max} . 254.5 m μ (log ϵ 3.94) and 329 (3.55), λ_{\min} . 233 (3.24) and 298 (2.44), λ_{\max} . 6.07br μ (Found: C, 56.1; H, 5.7; Cl, 16.6; N, 6.5. $C_{10}H_{12}ClNO_2$ requires C, 56.2; H, 5.7; Cl, 16.6; N, 6.6%). 7-Amino-8-hydroxy-1-tetralone melted at 82—83° (from hexane), λ_{\max} . (in EtOH) 240 m μ (log ϵ 4.23), 277 (3.94), and 381 (3.41), λ_{\min} . (in EtOH) 264 (3.84) and 314.5 (2.74), λ_{\max} . (in EtOH-HCl) 256 (3.98) and 325 (3.59), λ_{\min} . (in EtOH-HCl) 280 (2.79), λ_{\max} . 2.90, 2.99, and 6.17br μ (Found: C, 67.5; H, 6.1; N, 7.9%).

5,8-Dihydroxy-1-tetralone. The diazonium compound from 5-amino-8-hydroxy-1-tetralone was hydrolysed in 60% sulphuric acid at 138°, yielding 5,8-dihydroxy-1-tetralone, m. p. 179—181° (from heptane), λ_{\max} . 235.5 m μ (log ϵ 4.12), 266 (3.93), and 376 (3.61), λ_{\max} . 3.07br and 6.15 μ . Its infrared spectrum was identical with that of an authentic sample.⁴ The diacetate had m. p. 176.6—177.7° (from methanol) (lit.,⁴ 177—178°), and the phenylurethane had m. p. 177—178° (lit.,⁴ 181°).

7-Hydroxy-4-nitro-1-indanone. The mixture (22.1 g., 79%) of 7-hydroxy-4- and -6-nitro-1-indanone was obtained by treating 7-hydroxy-1-indanone (21.5 g.) in glacial acetic acid (200 ml.) with fuming nitric acid (14.3 ml.; d 1.49—1.50) at 15—22°. A solution of the mixture (5.25 g.) in benzene (150 ml.) was chromatographed on alumina (120 g.). 7-Hydroxy-4-nitro-1-indanone (2.55 g.), eluted with benzene (500 ml.) then ether (500 ml.), had m. p. 136.7—138.1° (from methanol) (Found: C, 55.7; H, 3.7; N, 7.2. $C_9H_7NO_4$ requires C, 56.0; H, 3.7; N, 7.3%). 7-Methoxy-4-nitro-1-indanone, obtained (76%) from reaction of the phenol with diazomethane in ether, had m. p. 191.6—192° (from methanol), λ_{\max} . 235 m μ (log ϵ 4.19), 253 (4.22), and 315 (4.05), λ_{\min} . 221 (4.05), 241 (4.15), and 272 (3.80) (Found: C, 58.1; H, 4.6; N, 6.7. $C_{10}H_9NO_4$ requires C, 58.0; H, 4.4; N, 6.8%).

7-Hydroxy-6-nitro-1-indanone. Further elution with ether (450 ml.) afforded a mixture of the 4- and 6-nitro-isomers (0.34 g.). The 6-nitro-derivative (1.60 g.), obtained on eluting the column with methylene chloride (500 ml.) then methanol (1000 ml.), had m. p. 147—148.6° (from methanol) (Found: C, 56.4; H, 3.5; N, 7.2%). 7-Methoxy-6-nitro-1-indanone was prepared similarly (66%), m. p. 113—114° (from methanol), λ_{\max} . 240 m μ (log ϵ 4.27), λ_{\min} . 221 (4.03) (Found: C, 57.9; H, 4.2; N, 6.9%).

¹⁵ Calvet and Carnero, *J.*, 1936, 556.

¹⁶ Thomson, Race, and Rowe, *J.*, 1947, 350.

7-Hydroxy-4,6-dinitro-1-indanone. The procedure employed in the preparation of 8-hydroxy-5,7-dinitro-1-tetralone afforded 7-hydroxy-4,6-dinitro-1-indanone (40%), m. p. 169—170.4° (from benzene), λ_{max} , 241 m μ (log ϵ 4.32) and 323 (3.74), λ_{min} , 241 (4.32) (Found: C, 45.7; H, 2.2; N, 12.0. $\text{C}_9\text{H}_6\text{N}_2\text{O}_6$ requires C, 45.4; H, 2.5; N, 11.8%). *7-Methoxy-4,6-dinitro-1-indanone* was obtained (71%) by treating the phenol in tetrahydrofuran with diazomethane, m. p. 101.2—102.4° (from methanol), λ_{max} , 226 m μ (log ϵ 4.30) (Found: C, 47.7; H, 3.3; N, 11.2. $\text{C}_{10}\text{H}_8\text{N}_2\text{O}_6$ requires C, 47.6; H, 3.2; N, 11.1%).

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542. Spectrophotometric Determination of Dissociation Quotients of Hydroxytriazens and the Effect of Substituents on pK Values.

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THE dissociation quotients of hydroxytriazens cannot be determined by conventional potentiometric and conductometric methods because of their very weak acidic nature. However, an observation that they develop an intense yellow colour in alkali suggested the possibility of using spectrophotometry for this purpose.

Ultraviolet absorption studies of these compounds have been made.¹ The absorption maximum at 348 m μ of 3-hydroxy-1,3-diphenyltriazene shifts to 390 m μ in alkali. This change in absorption maximum with pH is of use in determining the ionisation constants of hydroxytriazens.

Robinson and his collaborators²⁻⁵ have developed a spectrophotometric method for determining the degree of dissociation of weak acids in a buffer of known pH.

Outline of Spectrophotometric Method.—In acid it is assumed that the hydroxytriazene is all present as molecules and that at pH 14 it is all in the ionic form. Hence, it is reasonable to assume that the absorption peak at 348 m μ is to be ascribed to the unchanged hydroxytriazene molecule and the peak at 390 m μ to the anion. The molecular form of hydroxytriazene has negligible absorption at 390 m μ ; hence a measure of the absorbance at this wavelength for different pH values gives the extent of formation of the anion. The degree of ionisation, α , at a given pH, is thus given by:

$$\alpha = (A - A_a)/(A_b - A_a) \quad (1)$$

where A_a is absorbance of triazene in acid, where all of it is present as molecules, A_b is the absorbance in alkaline solution where all of it is present as anion, and A is the absorbance in a buffer solution of intermediate pH where a fraction, α , of the triazene is present as anion. The stoichiometric concentration of all these solutions is kept the same, and absorbance measurements are made at 390 m μ . The pK value of the acid is then given by:

$$\text{pK} = \text{pH} - \log_{10}[\alpha/(1 - \alpha)]$$

By use of this formula, pK values for different hydroxytriazens were determined.

¹ D. N. Purohit, Ph.D. Thesis, Rajasthan, Jaipur, 1963.

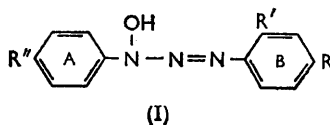
² Robinson, Abs. Symp., "Structure of Electrolytic Solutions," Washington, 1957, p. 90.

³ Bower and Robinson, *J. Phys. Chem.*, 1960, **64**, 1078.

⁴ Robinson, Davis, Paabo, and Bower, *J. Res. Nat. Bur. Stand.*, 1960, **64**, 347.

⁵ Davis, Paabo, and Robinson, *J. Res. Nat. Bur. Stand.*, 1960, **64**, 531.

Dissociation quotients of various hydroxytriazenes (I).



Compound			pK	Compound			pK
R	R'	R''		R	R'	R''	
H	H	H	11.41 ₄	H	H	Me	11.85 ₇
Cl	H	H	10.72 ₄	Me	H	Me	12.17 ₆
H	Cl	H	10.51 ₉	NHAc	H	H	11.66 ₃
H	H	Cl	10.64 ₈	CO ₂	H	H	10.97 ₂
Br	H	H	10.86 ₄	Ac	H	H	10.96 ₂
Me	H	H	11.78 ₃	OMe	H	H	10.95 ₄
H	Me	H	11.54 ₆	SO ₃ Na	H	H	9.98 ₈

Experimental.—Solutions. Hydroxytriazenes were prepared by adopting the method given by Sogani and Bhattacharya.⁶ Weighed amounts of these compounds were dissolved in dioxan to give 10⁻³M solutions; 1M-potassium chloride and 1N-sodium hydroxide were used for maintaining ionic concentration and for adjusting different pH values, respectively.

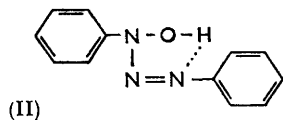
Apparatus. Absorbance measurements were made with a Beckmann Quartz spectrophotometer, model DU, and 1-cm. silica cells.

Procedure. A series of solutions containing different amounts of 1N-sodium hydroxide and 5.0 ml. of 1M-potassium chloride was prepared in 50-ml. volumetric flasks so that the pH of the final solutions ranged from 6 to 14 and the ionic concentration was 0.1M. They were suspended in a thermostat kept at 25°. In each case 1 ml. of 10⁻³M-triazene solution (freshly prepared) was added with a pipette, the solution diluted to the mark immediately and shaken. Absorbance was measured at 390 mμ.

The results obtained for different hydroxytriazenes are given in the Table.

DISCUSSION

Hydroxytriazenes are very weak acids, although on general grounds they would be expected to be stronger acids than phenol. The suppression of acid character may be attributed to the intramolecular hydrogen-bonded form (II) in which these compounds possibly exist.



A and B (I).

A comparison of the pK values of the methyl-substituted hydroxytriazenes (see Table) with the parent compound reveals that a methyl group at position 4 in ring B (I; R = Me, R' = R'' = H) increases the pK value by 0.369 units, and at position 4' in ring A (I; R = R' = H, R'' = Me) by 0.443 units. This is due to the +I effect (electron repelling) of the methyl groups. A hyperconjugative effect from the methyl group would also have a similar result. The methyl group has a greater influence on the N-OH nitrogen atom from ring A than from ring B, due to the distance factor. The lower acidity of 4,4'-dimethyl-N-hydroxytriazene (I; R = R'' = Me, R' = H) than either of the monomethyl isomers is quite reasonable in view of the arguments given above. The difference of 0.761 units between the pK values of 4,4'-dimethyl-N-hydroxytriazene and the unsubstituted hydroxytriazene happens to be approximately the sum of the difference between the pK values of the monomethyl isomers and that of the parent compound. The suppression of acidic character in 4-acetamidohydroxytriazene (I; R = NHAc, R' = R'' = H) is undoubtedly due to the +M (mesomeric) effect of the NHAc group, and as it is to that of the methoxy group in 4-methoxyhydroxytriazene (I; R = OMe, R' = R'' = H).

The chloro- and bromo-hydroxytriazene are more acidic than the parent. In these

⁶ Sogani and Bhattacharya, *Analyt. Chem.*, 1956, **28**, 81; *J. Indian Chem. Soc.*, 1959, **36**, 563.

compounds the $+M$ effect of chlorine is not evident due to the strong $+M$ effect of the $-N=N-$ group, and only the $-I$ effect of the halogens affects the dissociation of the hydroxytriazens. The bromine atom at position 4 in ring B (I; R = Br, R' = R'' = H) decreases the pK value of the parent hydroxytriazene by 0.550, which is less than that observed in the chloro-derivative (0.190 units). This seems to be quite reasonable in view of the fact that the inductive effect of halogens decreases in the order $F > Cl > Br > I$.

As stated earlier, the acidity of hydroxytriazene is suppressed by its intramolecular hydrogen-bonded structure, and so any factor that has a tendency to dislocate the hydrogen-bonding will naturally increase its acidity. Such an effect has been shown by the pK values of 2-methyl- and 2-chloro-substituted hydroxytriazens (I; R = R'' = H, R' = Me and Cl, respectively). The hydroxytriazene with a methyl group at position 2 in ring B (III; R' = Me, R = R'' = H) should be a weaker acid than its *p*-isomer due to the nearness of the $+I$ effect of the group on the *N*-OH nitrogen atom. However, the contrary is the case. The greater acidity of the *ortho*- than the *para*-isomer is due to the *ortho*-effect of the methyl group.

The pK values of the 2-chloro- (I; R' = Cl, R = R'' = H) and 4-chloro- (I; R' = R'' = H, R = Cl) substituted hydroxytriazens are less than that of the parent hydroxytriazene by 0.895 and 0.690 units, respectively. The strong ionising effect of chlorine at position 2 is due to the proximity of its $-I$ effect and the inhibition of hydrogen-bonding by virtue of its *ortho*-effect.

The strong acid character of hydroxytriazens with SO_3Na , CO_2H , and Ac at position 4 in ring B is due to the $-M$ effect of the groups. If pK values are in any way representative of the effect of groups, the ΔpK values 1.426 and 0.452 units are in decreasing order of the mesomeric effect of the groups, $SO_3Na > Ac$. In the case of 4- CO_2H -substituted hydroxytriazene the decrease in pK value is 0.442 units, which seems to be somewhat low. It can be explained on the basis that the compound has two dissociation constants, the first due to ionisation of $-CO_2H$ ($pK = 6.52$), and second due to ionisation of OH ($pK = 10.97_2$). The removal of a proton from a negative ion is difficult, so that the pK_{OH} is rather high.

The authors are grateful to Professor R. C. Mehrotra for providing facilities in the Department, and to Drs. D. S. Deorha and M. M. Bokadia for their keen interest in the investigation. One of us (D. N. P.) thanks the University Grants Commission for a research scholarship.

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543. Compounds of Cobalt(III) with Induced Asymmetry.

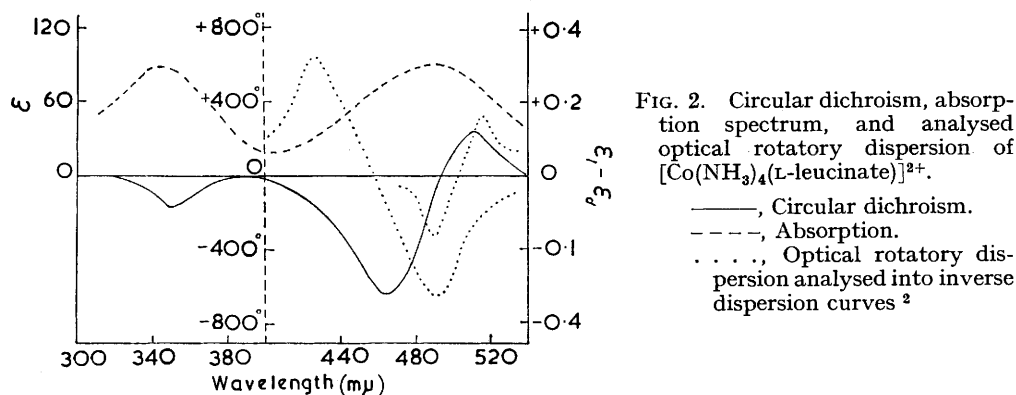
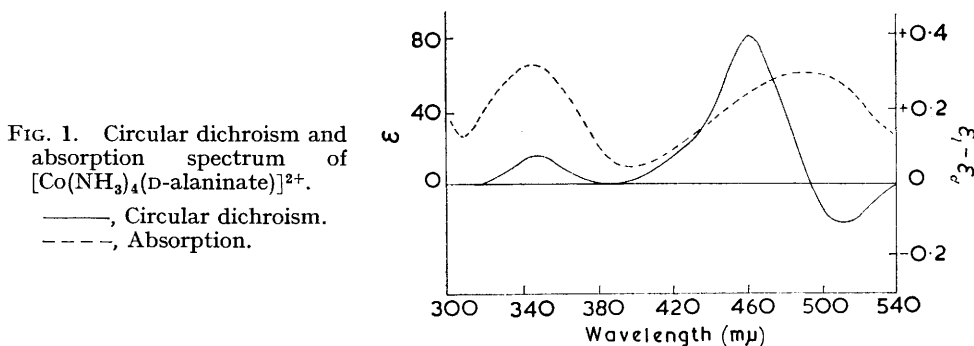
By J. H. DUNLOP and R. D. GILLARD.

COMPOUNDS of the type $D-[Co en_2(L\text{-amino-acid})]^{2+}$, where en = ethylenediamine, show ¹ a marked rotational strength for the longest-wavelength transition around 500 $m\mu$, as might be expected in view of the asymmetry of the cation as a whole. The analogous compounds $[Co(NH_3)_4(L\text{-amino-acid})]^{2+}$ develop optical activity in their $d-d$ bands, simply owing to the asymmetry introduced by the asymmetric carbon atom of the ligand. The circular dichroisms of the cations (*D*-alaninato)tetramminecobalt(III), (*L*-leucinato)tetramminecobalt(III), and (*L*-histidinato)tetramminecobalt(III) are shown, with absorption spectra, in Figs. 1—3. By analysing the optical rotatory dispersion curve of the *L*-leucine compound, Shimura deduced ² that band I gave rise to two Cotton effects, of opposite sign (shown in Fig. 2), agreeing well with the result from circular dichroism.

¹ Mathieu, *Bull. Soc. chim. France*, 1939, **6**, 873; Lifschitz, *Rec. Trav. chim.*, 1939, **58**, 785.

² Shimura, *Bull. Chem. Soc. Japan*, 1958, **31**, 315.

Complexes of cobalt(III) with O_h symmetry give rise to two $d-d$ transitions, ${}^1T_{1g} \leftarrow {}^1A_{1g}$ (band I) and ${}^1T_{2g} \leftarrow {}^1A_{1g}$ (band II). Band I is magnetic-dipole-allowed (and therefore strongly optically active), whereas band II, at lower wavelength, is not. While lowering the symmetry of the ion gives rise to splitting of both bands I and II, the selection rules for O_h still control the relative rotational strengths of the components. Thus, in complexes with D_3 symmetry, both components of band I (${}^1E_g + {}^1A_{1g}$) are magnetic-dipole-allowed; although their rotational strengths are of opposite sign, the resultant circular dichroism is much more marked than that of band II, where only the E_g component is magnetic-dipole-allowed. Under favourable circumstances, the character of transitions in



optically active molecules can be deduced from the g -value, which is greater than 10^{-2} for magnetic-dipole and less than 10^{-2} for electric-dipole-allowed transitions. However, in the complexes of amino-acids examined here, the circular dichroism maxima for band I are residual "wing" absorptions [as they are³ in complexes of rhodium(III) with D_3 symmetry], so that the maximal g value for each component cannot be determined; the "wing" absorptions result from the overlap of circular dichroism maxima of opposite signs. However, the circular dichroism in band II is due to a single component, a typical g -value (for the alanine complex) being 0.002. While this is formally a magnetic-dipole-allowed transition, the parent transition (in O_h) is magnetic-dipole-forbidden, and the selection rules for O_h are still strong. (This is also clear from the fact that oscillator strengths of centrosymmetric complexes of cobalt(III) are comparable with those of non-centrosymmetric complexes.) This is the reason for the experimental observation⁴ that the optical rotatory dispersion curves of cobalt(III) complexes in the visible region can be interpreted by considering band I only, band II having very little effect.

³ Dunlop and Gillard, *J.*, 1964, in the press.

⁴ Burer, *Helv. Chim. Acta*, 1963, **46**, 242, and references therein.

A further point of value is that configurations of amino-acids are readily compared. Acids of the same configuration give rise to an asymmetric potential at the cobalt atom of the same sign, and hence give Cotton effects of the same sign for corresponding $d-d$ bands of $[\text{Co}(\text{NH}_3)_4(\text{amino-acid})]^{2+}$. This is reminiscent of the configurational comparisons by Pfeiffer and others⁵ using complexes of copper(II). However, the complexes of cobalt(III) are more satisfactory as their chemistry and spectra are more fully known.

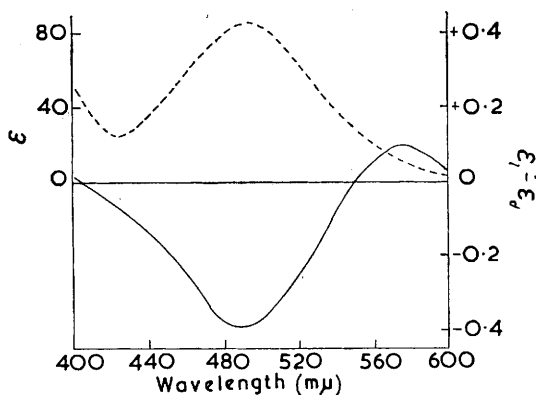
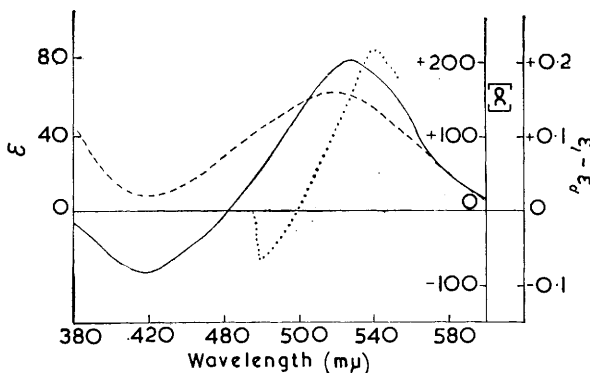


FIG. 3. Circular dichroism and absorption spectrum of $[\text{Co}(\text{NH}_3)_4(\text{L-histidinate})]^{2+}$.

—, Circular dichroism.
- - - , Absorption.

FIG. 4. Circular dichroism, absorption spectrum, and optical rotatory dispersion of

$[\text{Co}(\text{NH}_3)_4(+\text{-tartrate})]^{2+}$
—, Circular dichroism.
- - - , Absorption.
... , Optical rotatory dispersion⁶



The optical rotatory dispersion⁶ for band I of $[(+)\text{-tartrato}]$ tetramminecobalt(III) cation shows a single Cotton effect; however, the circular dichroism (Fig. 4) reveals two components of opposite sign. It seems to be a general rule that the rotational strength of band I in octahedral complexes of cobalt(III) (measured either by the amplitude of the Cotton curve in optical rotatory dispersion, or by the maximum circular dichroism) is dependent on the number of chelate rings in the molecule, compounds with one chelate ring having $(\epsilon_l - \epsilon_d)$ about 0.4, those with two chelate rings about 0.9, and those with three chelate rings about 1.8.

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⁵ Pfeiffer, *Ber.*, 1944, **75**, 57.

⁶ Albinak, Bhatnagar, Kirschner, and Sonnessa, *Canad. J. Chem.*, 1961, **39**, 2360.

544. 2-Hydroxy-3-methyl- and 3-Hydroxy-2-methyl-1,4,6-triazanaphthalene; a Correction.

By J. W. CLARK-LEWIS and R. P. SINGH.

CONDENSATION of ethyl pyruvate with 3,4-diaminopyridine gives a mixture of 3-hydroxy-2-methyl-, m. p. 276—278° (decomp.), and 2-hydroxy-3-methyl-1,4,6-triazanaphthalene, m. p. 262—263° (decomp.). These orientations of substituents were established by methylation, although under "2-hydroxy-3-methyl-1,4,6-triazanaphthalene" in the Experimental section of our earlier Paper¹ the isomers were inadvertently transposed. The corrected orientations agree with those assigned on other grounds by Albert and Barlin,² and are confirmed by the occurrence of the 5-H n.m.r. signal at lower field in the 2-hydroxy-isomer (τ 1.17) than in 3-hydroxy-2-methyl-1,4,6-triazanaphthalene (τ 1.38). Similarly, the 5-H signal in 1,2-dihydro-1,3-dimethyl-2-oxo-1,4,6-triazanaphthalene occurs at lower field (τ 1.04) than in the 2,4-dimethyl-3-oxo isomer (τ 1.32).

Experimental.—Nuclear magnetic resonance spectra were recorded with a Varian D.P. instrument at 60 Mc./sec. with tetramethylsilane as internal standard.

τ -Values for 2-hydroxy-3-methyl-1,4,6-triazanaphthalene in dimethyl sulphoxide were: 5-H, 1.17; 7-H, 1.55; and 8-H, 2.81; and those for 3-hydroxy-2-methyl-1,4,6-triazanaphthalene in dimethyl sulphoxide were: 5-H, 1.38; 7-H, 1.59; and 8-H, 2.38. τ -Values for 1,2-dihydro-1,3-dimethyl-2-oxo-1,4,6-triazanaphthalene (m. p. 141—142°, incorrectly reported¹ as 276—277°), prepared from 3-amino-4-methylamino-pyridine, in carbon tetrachloride were: 5-H, 1.04; 7-H, 1.44; 8-H, 2.90; *N*-Me, 6.38; *C*-Me, 7.43; and those for 3,4-dihydro-2,4-dimethyl-3-oxo-1,4,6-triazanaphthalene (m. p. 114—115°, incorrectly reported¹ as 228—230°), prepared from 4-amino-3-methylaminopyridine, in carbon tetrachloride: 5-H, 1.32; 7-H, 1.51; 8-H, 2.44; *N*-Me, 6.29; and *C*-Me, 7.44.

We thank Professor A. Albert and Dr. G. B. Barlin for samples of the hydroxytriazanaphthalenes and for discussion of their orientations. We are grateful to Dr. T. M. Spotswood for the n.m.r. spectra.

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[Received, October 26th, 1963.]

¹ Clark-Lewis and Singh, *J.*, 1962, 3162.

² Albert and Barlin, *J.*, 1963, 5156.

545. Photochemically-induced Substitution Reactions of Pentacarbonyliron.

By J. LEWIS, R. S. NYHOLM, S. S. SANDHU, and M. H. B. STIDDARD.

SEVERAL methods have been described for the preparation of substitution compounds of pentacarbonyliron: direct reaction of the ligand with pentacarbonyliron,¹⁻⁴ bis(cyclopentadienyldicarbonyliron),⁵ or cyclo-octatetraenetricarbonyliron⁴ in the absence of solvent, or with duodecacarbonyltri-iron in solution.^{6,7} We now describe a further method whereby substitution in pentacarbonyliron is initiated photochemically.

The monodentate ligands PPh₃ and AsPh₃ react readily with pentacarbonyliron in cyclohexane, on exposure to ultraviolet (u.v.) light, to produce mixtures of complexes of the

¹ Reppe and Schweckendick, *Annalen*, 1948, 560, 104.

² Cotton and Parish, *J.*, 1960, 1440.

³ Nigam, Nyholm, and Ramana Rao, *J.*, 1959, 1397.

⁴ Manuel, *Inorg. Chem.*, 1963, 2, 854.

⁵ Hallam and Pauson, *J.*, 1956, 3030.

⁶ Clifford and Mukherjee, *Inorg. Chem.*, 1963, 2, 151.

⁷ Sandhu, Thesis, London, 1963.

type $\text{Fe}(\text{CO})_4\text{L}$ and $\text{Fe}(\text{CO})_3\text{L}_2$, which have been separated by methods dependent upon their differing volatilities and solubilities. Their physical properties, summarised in the Table are clearly consistent with their formulations and, where these have been measured previously, agree with published data.

Properties of carbonyliron complexes.

Complex *	M. p.	C-O stretching frequencies (cm^{-1} in CHCl_3) †	M (Found)	M (Calc.)
$\text{Fe}(\text{CO})_4\text{PPh}_3$	201—203°	2045, 1965, 1927	428 ‡	430
$\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$	268—270	1873	617 §	664
$\text{Fe}(\text{CO})_4(\text{AsPh}_3)$	160—161	2041, 1961, 1923	448 ‡	474
$\text{Fe}(\text{CO})_3(\text{AsPh}_3)_2$	170—172	1876	695 §	752
$[\text{Fe}(\text{CO})_4]_2(\text{Diphos})$	170—172	2053, 1980, 1938	697 §	734
$\text{Fe}(\text{CO})_3(\text{Diphos})$	136—137	1996, 1923, 1898	488 §	538
$\text{Fe}(\text{CO})_3(\text{Diars})$	131—132	1996, 1916, 1887	401 ‡	426

* All complexes are diamagnetic and a representative selection was found to be non-electrolytes in PhNO_2 . † All bands are strong. ‡ Cryoscopic in C_6H_6 . § Isopiestic in C_6H_6 .

The bidentate diphosphine 1,2-bisdiphenylphosphinoethane (Diphos) reacts with pentacarbonyliron under similar conditions to produce the complex $[\text{Fe}(\text{CO})_4]_2(\text{Diphos})$, in which the ligand atoms are co-ordinated to separate iron atoms. The tendency for this type of bridged compound to be formed under u.v. irradiation has been noted previously.⁸ Further, the identical compound has been prepared recently by Manuel⁴ by direct reaction of the diphosphine with pentacarbonyliron. Conversion from the bridged into the chelate complex $\text{Fe}(\text{CO})_3(\text{Diphos})$ can be effected readily by heating the former *in vacuo* at about 150°. *o*-Phenylenebisdimethylarsine (Diars) also reacts with pentacarbonyliron, under the influence of u.v. light, to yield the product $\text{Fe}(\text{CO})_3(\text{Diars})$.³ Some spectroscopic evidence for the formation of the bridged complex $[\text{Fe}(\text{CO})_4]_2(\text{Diars})$ was also obtained, but the pure compound could not be isolated.

Experimental.—*Tetracarbonyltriphenylphosphineiron(0)*. A solution of pentacarbonyliron (3 ml.) and triphenylphosphine (2.2 g.) in cyclohexane (18 ml.) was exposed to u.v. light for 12 hr. A mixture of golden plates of the carbonyl $\text{Fe}_2(\text{CO})_9$ and a yellow solid was slowly formed. The latter was separated by dissolution in dichloromethane. Evaporation of the solvent, followed by washing the remaining solid with ethanol, yielded a mixture of the mono- and di-substituted compounds. The separation of the complex (0.85 g.) was effected by sublimation *in vacuo* at 180° (Found: C, 61.6; H, 3.3; P, 7.3. $\text{C}_{22}\text{H}_{15}\text{O}_4\text{PFe}$ requires C, 61.4; H, 3.3; P, 7.2%). This compound, like those described below, is soluble in aromatic solvents, chloroform, and dichloromethane, but insoluble in light petroleum.

Tricarbonylbis(triphenylphosphine)iron(0). The residue from the above sublimation was purified by crystallisation from cyclohexane–dichloromethane to yield the pure compound (0.62 g.), which was dried *in vacuo* (Found: C, 70.4; H, 4.5; P, 8.7. $\text{C}_{39}\text{H}_{30}\text{O}_3\text{P}_2\text{Fe}$ requires C, 70.5; H, 4.5; P, 9.3%).

Tetracarbonyltriphenylarsineiron(0). A solution of pentacarbonyliron (3 ml.) and triphenylarsine (2.1 g.) in cyclohexane (15 ml.) was exposed to u.v. light for 9 hr., a yellow crystalline solid separating. This was filtered off, washed with cyclohexane, and dried *in vacuo*. Extraction with warm cyclohexane and subsequent concentration and cooling yielded the pure compound (0.8 g.), which was dried *in vacuo* (Found: C, 55.9; H, 3.3; As, 16.1; Fe, 11.3. $\text{C}_{22}\text{H}_{15}\text{AsO}_4\text{Fe}$ requires C, 55.7; H, 3.2; As, 15.8; Fe, 11.8%).

Tricarbonylbis(triphenylarsine)iron(0). The residual solid from the above extraction was further extracted with dichloromethane. Evaporation of the solvent produced a solid, which was purified by crystallisation from dichloromethane–light petroleum to yield the compound (0.32 g.), which was dried *in vacuo* (Found: C, 62.3; H, 4.1; As, 19.8; Fe, 7.6. $\text{C}_{39}\text{H}_{30}\text{As}_2\text{O}_3\text{Fe}$ requires C, 62.2; H, 4.0; As, 20.0; Fe, 7.5%).

Octacarbonyl- $\mu\mu'$ -1,2-bisdiphenylphosphinoethane-di-iron(0). A mixture of pentacarbonyliron (2.3 ml.) and the diphosphine (0.51 g.) in cyclohexane (10 ml.) was exposed to u.v. light for 15 hr., the tube being shaken occasionally. The crude solid was dissolved in the minimum volume of

⁸ Nyholm, Sandhu, and Stiddard, *J.*, 1963, 5916.

dichloromethane. Filtration and concentration under reduced pressure yielded the pure *compound* (0.76 g.) which was dried *in vacuo* (Found: C, 55.4; H, 3.6; P, 8.35. $C_{32}H_{24}O_8P_2Fe_2$ requires C, 55.6; H, 3.3; P, 8.45%).

Tricarbonyl-1,2-bisdisphenylphosphinoethaneiron(0). The aforementioned compound $[Fe(CO)_4]_3$ (Diphos) (0.86 g.) was heated in an evacuated tube at 150–160° for 8 hr. The tube was carefully opened, evacuated, resealed, and heated at the same temperature for a further 8 hr. After being washed with hot petroleum, the product was dissolved in benzene. Concentration under reduced pressure produced the *compound* (0.35 g.) which was dried *in vacuo* (Found: C, 65.1; H, 4.6; P, 11.8. $C_{29}H_{24}O_3P_2Fe$ requires C, 64.7; H, 4.5; P, 11.5%).

Tricarbonyl-o-phenylenebisdimethylarsineiron(0). A solution of pentacarbonyliron (3 ml.) and the diarsine (1.5 ml.) in cyclohexane (10 ml.) was exposed to u.v. light for 18 hr. The solution was filtered and the solvent evaporated completely to leave an oily liquid. The solid, formed on addition of ether, was recrystallised from benzene–light petroleum to yield the *compound* (0.21 g.), which was dried *in vacuo* (Found: C, 36.7; H, 3.6; As, 35.8; Fe, 12.4. $C_{13}H_{16}As_2O_3Fe$ requires C, 36.6; H, 3.8; As, 35.2; Fe, 13.2%).

Photochemical reactions. These were carried out in evacuated Pyrex tubes (12 in. length \times 1 in. diameter), the source being an 80 w mercury lamp.

Iron analyses. The iron contents of some of the compounds described were determined by ignition to the oxide, Fe_2O_3 . Compounds containing phosphorus could not be analysed in this way.

We are indebted to the Commonwealth Scholarship Commission and E. I. du Pont de Nemours (U.S.A.) for maintenance grants (to S. S. S.).

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546. *Reactions of Pentafluorophenol with Titanium Tetrachloride.*

By V. S. V. NAYAR and R. D. PEACOCK.

UNDER suitable conditions, phenol reacts with titanium tetrachloride to give compounds of composition $Ti(C_6H_5O)Cl_3$,¹ $Ti(C_6H_5O)_3Cl$,² and $Ti(C_6H_5O)_4$.^{2,3} We now find that pentafluorophenol reacts with titanium tetrachloride and causes substitution and hydrogen chloride evolution at 25°. When excess of pentafluorophenol is used, the main product is a deep red liquid from which the tetraphenoxy-compound $Ti(C_6F_5O)_4$ is isolated as orange-red crystals, m. p. 165–167° [compare $Ti(C_6H_5O)_4$, m. p. 155°]. The compound volatilises under a high vacuum at 150°, and begins to decompose at 200°. With excess of titanium tetrachloride the main product is the red-brown crystalline compound $Ti(C_6F_5O)_2Cl_2$, m. p. 98–100°, which volatilises under a high vacuum at 40–50°. A small quantity of a more volatile red glass, which appears to contain the monosubstituted derivative $Ti(C_6F_5O)Cl_3$, is also formed. These compounds, like titanium tetrachloride itself and the hydrogen aromatic derivatives, are rapidly hydrolysed in moist air; the products are titanium dioxide and pentafluorophenol. It is interesting that no reaction takes place between the tetrakis-pentafluorophenoxide and titanium tetrachloride, and that the action of pentafluorophenol on bis-pentafluorophenoxydichlorotitanium leads only to the tetrakis-pentafluorophenoxide.

The properties (melting point and volatility) of the two pentafluorophenoxy-compounds suggest that the titanium atoms retain four-co-ordination, *i.e.*, they are roughly in line with those of the binary halides, other than the fluoride, arranged in order of molecular weight. Nevertheless, the tetrakis-pentafluorophenoxide forms an unstable volatile solvate with excess of pentafluorophenol; in this the titanium must be 5- or 6-co-ordinate, and the enhanced volatility is perhaps associated with decreased molecular interaction.

¹ Luchinski and Altman, *Z. anorg. Chem.*, 1935, **225**, 321.

² Varma and Mehrotra, *J. Indian Chem. Soc.*, 1961, **38**, 147.

³ Hanic, *Chem. listy*, 1956, **49**, 370.

Infrared absorption peaks (cm^{-1}) from 800 to 400 cm^{-1} .

$\text{C}_6\text{F}_5\text{OH}$	750m, 610m, 565m, 450m
$\text{Ti}(\text{C}_6\text{F}_5\text{O})_4$	790vw, 730s, 715, 668m, 635m, 585m, 575m, 515vs, 490m, 450 m, 410m
$\text{Ti}(\text{C}_6\text{F}_5\text{O})_2\text{Cl}_2$	750m, 720w, 665w, 500m, 450w, 420m

In the sodium chloride region the infrared spectra of the compounds are very similar to the corresponding spectrum of pentafluorophenol, but in the potassium bromide region (800—400 cm^{-1}) there are differences (see Table). Some of the additional peaks are presumably associated with Ti-O and Ti-Cl vibrations; for example, a peak at 500 cm^{-1} in bispentafluorophenoxydichlorotitanium is close to a double peak in titanium tetrachloride ($\nu_3 = 490, 506 \text{ cm}^{-1}$).⁴ However, not enough data are available to make certain assignments.

Debye X-ray powder photographs confirm the individuality of the compounds, but are too complicated to be indexed.

Experimental.—Titanium tetrachloride (reagent grade) was redistilled twice under a vacuum, the head and tail fractions being rejected before use. Pentafluorophenol was prepared by the method of Birchall and Haszeldine.⁵

Infrared spectra were measured on a Perkin-Elmer Infracord spectrophotometer, using potassium bromide optics. Specimens were milled with Nujol in a dry-box. X-Ray spectra were measured with a 19-cm. camera, using Cu K_α radiation.

Reaction of titanium tetrachloride with excess of pentafluorophenol. Titanium tetrachloride was condensed under a vacuum into a bulb containing an excess (about 3 : 1 by volume) of pentafluorophenol at -75° . After dry nitrogen had been admitted, the mixture was allowed to warm to room temperature. Gas evolution began immediately, the titanium tetrachloride melted, and a dark red liquid was formed. When evolution of hydrogen chloride had ceased, the excess of pentafluorophenol was pumped off, and the temperature of the residue was raised slowly. At 50—60° a red liquid distilled; this was a solvate of $\text{Ti}(\text{C}_6\text{F}_5\text{O})_4$ which, above 60°, lost pentafluorophenol, to leave pure *tetrakis(pentafluorophenoxy)titanium(IV)* [Found: Ti, 5.9; ($\text{C}_6\text{F}_5\text{O}$), 92.4; C, 33.5; F, 48.7. $\text{Ti}(\text{C}_6\text{F}_5\text{O})_4$ requires Ti, 6.1; ($\text{C}_6\text{F}_5\text{O}$), 93.8; C, 36.9; F, 48.7%]. The compound distilled under a vacuum at 160—170°. A violet residue, which contained titanium(III), remained in the reaction bulb.

Reaction of pentafluorophenol with excess of titanium tetrachloride. Pentafluorophenol was treated with excess of titanium tetrachloride, using the same technique as above. After the excess of titanium tetrachloride had been pumped off at 25° the temperature was raised to about 60°. *Bispentafluorophenoxydichlorotitanium(IV)* sublimed [Found: Ti, 9.6; ($\text{C}_6\text{F}_5\text{O}$), 74.3; Cl, 14.2. $\text{Ti}(\text{C}_6\text{F}_5\text{O})_2\text{Cl}_2$ requires Ti, 9.9; ($\text{C}_6\text{F}_5\text{O}$), 75.4; Cl, 14.6%]. A violet residue, which contained titanium(III) remained in the reaction bulb.

Analysis. The compounds were broken down by dissolution in water. Titanium was estimated colorimetrically by the hydrogen peroxide method, chlorine gravimetrically as silver chloride, and ($\text{C}_6\text{F}_5\text{O}$) by titration against 0.1N-sodium hydroxide (phenolphthalein). Carbon and fluorine were estimated by standard methods after dry combustion.

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⁴ Hawkins and Carpenter, *J. Chem. Phys.*, 1955, **23**, 1700.

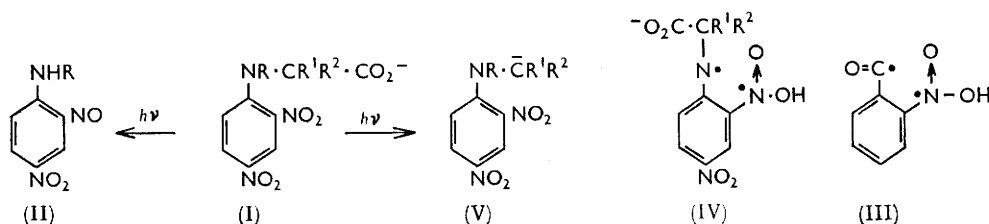
⁵ Birchall and Haszeldine, *J.*, 1959, 13.

547. *The Photochemical Degradation of N-2,4-Dinitrophenylamino-acids and Related Compounds. Part II.¹ Photolysis of N-2,4-Dinitrophenyl-N-methyl-leucine.*

By D. W. RUSSELL.

MILDLY alkaline solutions of *N*-2,4-dinitrophenyl derivatives of leucine¹ or other α -amino-acids,² when exposed to light, decompose, forming 4-nitro-2-nitrosoaniline (II; R = H). When such a solution of *N*-2,4-dinitrophenyl-*N*-methyl-leucine (I; R = Me, R¹ = H, R² = Bu¹) was illuminated, β -methylbutyraldehyde was formed, together with a green crystalline compound, C₇H₇N₃O₃, that responded to tests for a nitroso-group and gave 2,4-dinitro-*N*-methylaniline on mild oxidation. Its ultraviolet spectrum was very similar to that of 4-nitro-2-nitrosoaniline,¹ and we may conclude that the new compound is *N*-methyl-4-nitro-2-nitrosoaniline (II; R = Me). The initial rates of photolysis¹ of the leucine and *N*-methyl-leucine derivatives in dilute solution were identical.

Photochemical rearrangement of *o*-nitrosobenzaldehyde to *o*-nitrobenzoic acid³ is thought to proceed by initial abstraction of the aldehyde hydrogen atom by the photo-activated nitro-group, to form the species (III), and similar mechanisms have been postulated for related reactions.⁴ The present work shows that photolysis of an *N*-2,4-dinitrophenylamino-acid proceeds whether the amino-nitrogen bears a hydrogen atom or a methyl



group; the rates are similar and the products homologous. The presumably common reaction mechanism differs, therefore, from that suggested for the *o*-nitrosobenzaldehyde rearrangement, and does not involve the corresponding species (IV). Abstraction of hydrogen from the α -carbon atom is also excluded, since *N*-2,4-dinitrophenyl- α -phenyl- α -alanine (I; R = H; R¹ = Me; R² = Ph) yields 4-nitro-2-nitrosoaniline (II; R = H) on photolysis.²

An alternative mechanism might involve decarboxylation as the first step, to give the carbanion (V). This may seem unlikely, for the carboxyl group is effectively "insulated"⁵ from that part of the molecule which absorbs radiation at the photoactive wavelengths.¹ Nevertheless, in the dry state *N*-2,4-dinitrophenyl derivatives of α -amino-acids are photochemically decarboxylated,⁶ a reaction whose mechanism is equally obscure. Insulation of the carboxyl group in such compounds is probably incomplete. Titration, which presumably involves this group, results in minor ultraviolet spectral shifts.⁷ These, perhaps significantly, are considerably smaller in the photostable *N*-2,4-dinitrophenyl derivatives

¹ Part I, Russell, *J.*, 1963, 894.

² Russell, *Biochem. J.*, 1963, 87, 1.

³ Cimician and Silber, *Ber.*, 1901, 34, 2040.

⁴ de Mayo and Reid, *Quart. Rev.*, 1961, 15, 393.

⁵ P. de Mayo, personal communication.

⁶ Pollara and Von Korff, *Biochim. Biophys. Acta*, 1960, 39, 364.

⁷ Ramachandran and Sastry, *Biochemistry*, 1962, 1, 75.

of ω -amino-acids and of tryptophan² than in the photolabile derivatives of α -amino-acids generally.⁷ It is suggested that formation of the carbanion (V), by an undefined mechanism, may be the first and key step in photolysis of α -N-2,4-dinitrophenylamino-acids in mildly alkaline solution. The observed products could result from decomposition of the carbanion by more than one route, and a choice is not yet possible.

Experimental.—Melting points are corrected. Infrared and ultraviolet spectra, and rates of photolysis, were measured as before.¹

Photolysis of N-2,4-dinitrophenyl-N-methyl-leucine. The amino-acid derivative⁸ (0.25 g.) in 1% (w/v) sodium hydrogen carbonate solution (40 ml.) was illuminated for 20 hr. in the small apparatus previously described,¹ without stirring. The precipitate (0.12 g.) of *N-methyl-4-nitro-2-nitrosoaniline* (II; R = Me) formed green prisms (0.08 g.) (from acetone-water, 6 : 4), m. p. 165—167° (decomp.), λ_{\max} 287, 358, 449, 685 m μ (log ϵ 4.25, 4.11, 3.76, 1.82), ν_{\max} (film) 3220w, 1620m (N-H), 1510w (N-O?), 1490m (NO₂), 1415w (N-Me), 1370m (NO₂), 1330s (N-H) cm.⁻¹ [Found: C, 46.4; H, 4.5; N, 23.0; O, 26.4%; *M* (micro-Rast), 190, 196. C₇H₇N₃O₃ requires C, 46.4; H, 3.9; N, 23.2; O, 26.5%; *M*, 181].

The compound had solubility properties similar to those of 4-nitro-2-nitrosoaniline,¹ and it was extracted into ethyl acetate from dilute hydrochloric acid or dilute potassium carbonate solution. When warmed with 2*N*-sodium hydroxide it evolved basic vapours, and it gave positive tests for a nitroso-group. Thus, with *NN'*-diphenylbenzidine in sulphuric acid it gave a blue colour,⁹ its solution in glacial acetic acid turned deep orange-red when boiled with aniline,¹⁰ and its cherry-red solution in sulphuric acid became green when warmed with phenol.¹¹

The filtrate from the photolysed solution, when acidified and treated with 2,4-dinitrophenylhydrazine solution, gave β -methylbutyraldehyde 2,4-dinitrophenylhydrazone (0.11 g.).

Oxidation of N-methyl-4-nitro-2-nitrosoaniline. The nitroso-compound (II; R = Me) (0.053 g.) in glacial acetic acid (1 ml.) and 30% hydrogen peroxide (0.5 ml.) was boiled for 10 min., and the mixture was cooled and diluted with water (5 ml.). The orange precipitate gave *N-methyl-2,4-dinitroaniline* (0.032 g.), prisms (from acetone-water), m. p. 176—178°, mixed m. p. 176—177°. The infrared and ultraviolet spectra were identical with those of a reference sample.

I am grateful to Dr. V. M. Clark, Professor P. de Mayo, and Dr. T. L. V. Ulbricht for helpful discussions.

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⁸ Plattner and Nager, *Helv. Chim. Acta*, 1948, **31**, 2203; Russell, *J.*, 1962, 753.

⁹ Anger, *Mikrochim. Acta*, 1959, 387; 1960, 58.

¹⁰ Baeyer, *Ber.*, 1874, **7**, 1639.

¹¹ Liebermann, *Ber.*, 1874, **7**, 247.

548. 6α - and 6β -Nitrocholest-4-en-3-one.

By M. DAVIS.

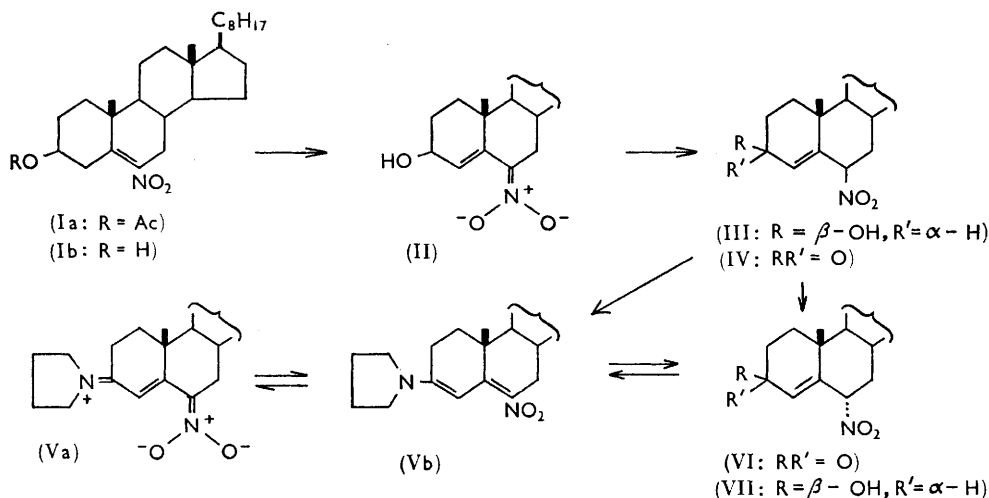
TANABE AND HAYASHI¹ obtained amorphous 6α -nitrocholest-4-en-3-one by dehydrochlorination of 5-chloro- 6β -nitro-5 α -cholestan-3-one. It exhibited the expected spectral characteristics and was partially converted into cholest-4-ene-3,6-dione by chromatography on silica gel or alumina. Since we had earlier prepared crystalline 6α - and 6β -nitrocholest-4-en-3-one by the procedure developed by Bowers *et al.*² in the androstane and pregnane series, we now report our results.

¹ Tanabe and Hayashi, *Chem. and Pharm. Bull. (Japan)*, 1962, **10**, 1177.

² Bowers, Sanches, and Ringold, *J. Amer. Chem. Soc.*, 1959, **81**, 3702.

Hydrolysis of 6-nitrocholesteryl acetate (Ia) with 2% methanolic potassium hydroxide afforded 6 β -nitrocholest-4-en-3 β -ol (III), also obtained by alkaline rearrangement of 6-nitrocholesterol (Ib). Protonation of the anion (II), formed in strongly alkaline solution, is kinetically controlled and should occur from the least-hindered α -face to give the thermodynamically less stable β -epimer.² This assignment is supported by subsequent reactions, by molecular-rotation evidence, and by the later preparation of what is probably the 6 α -epimer (VII).

Oxidation of the 6 β -nitro-alcohol (III) by the method of Jones and his co-workers³ yielded 6 β -nitrocholest-4-en-3-one (IV), which was readily isomerised by 0.5% methanolic potassium hydroxide, by way of the enolate, to the equatorial 6 α -epimer (VI). As pointed out by Bowers *et al.*,² the lower concentration of the *aci*-form in dilute alkali allows this



thermodynamically favoured conversion to occur. The α -ketone had λ_{max} 234 $\text{m}\mu$ (ϵ 14,300), and ν_{max} 1682, 1620, 1546, and 1369 cm^{-1} , in reasonable agreement with the values of 232 $\text{m}\mu$ (ϵ 13,900) and 1692, 1626, and 1558 cm^{-1} recorded by Tanabe and Hayashi¹ for their crude product. Sodium borohydride reduction of the 6 β -nitro-ketone regenerated the alcohol (III), whilst similar treatment of the 6 α -nitro-ketone afforded what is probably 6 α -nitrocholest-4-en-3 β -ol (VII), although it was not obtained crystalline.

Molecular rotations, M_D , of 6-nitro-derivatives.

Compound	6 α	6 β	ΔM_D	Compound	6 α	6 β	ΔM_D
Cholest-4-en-3-one	+326°	-442°	768°	Pregn-4-ene-3,20-dione *	+556°	-180°	736°
Androst-4-en-17 β -ol-3-one *	+97	-483	580	Cholest-4-en-3 β -ol	+121†	-446	567
Androst-4-ene-3,17-dione *	+483	-166	649	Androst-4-ene-3 β ,17 β -diol *	+157	-444	601

* Data from ref. 2. † Amorphous product; see Experimental.

Both ketones (IV) and (VI) gave the same red pyrrolidine enamine (Vb). The normal position of the strong nitro-band in the infrared spectrum makes it unlikely that the dipolar form (Va) contributes significantly to the structure. Molecular rotations (see Table) show the striking differences between 6 α - and 6 β -nitro-epimers, already noted in the androstane and pregnane analogues.²

³ Bowers, Halsall, Jones, and Lemin, *J.*, 1953, 2548.

Experimental.—Optical rotations were measured for chloroform solutions.

6-Nitrocholesterol. This was prepared by hydrolysis of the acetate with aqueous ethanolic hydrochloric acid, and had m. p. 121—123°, $[\alpha]_D -61^\circ$ (*c* 2.06), $M_D -262^\circ$ (Found: C, 75.1; H, 10.4; N, 3.15. Calc. for $C_{27}H_{45}NO_3$: C, 75.1; H, 10.5; N, 3.25%). The *methanesulphonate* had m. p. 139—141° (from ethanol), $[\alpha]_D -44^\circ$ (*c*, 1.98) (Found: S, 6.4. $C_{28}H_{47}NO_5S$ requires S, 6.3%).

6 β -Nitrocholest-4-en-3 β -ol. (a) 6-Nitrocholesteryl acetate (20 g.) was added in small portions to a refluxing solution of potassium hydroxide (6 g.) in methanol (300 ml.) under nitrogen. After 1 hr., acetic acid (8 ml.) and water (300 ml.) were added, and the suspension was extracted with ether (3 \times 200 ml.). The washed and dried extracts were concentrated, and diluted with methanol, giving the *nitro-compound* (10.22 g., 56%), m. p. 151—152° (from ether—light petroleum), $[\alpha]_D -103.5^\circ$ (*c* 2.0), $M_D -446^\circ$, u.v. spectrum shows end-absorption only, $\nu_{max.}$ (KBr) 3350 (OH), 1542 and 1362 (NO_2) cm^{-1} (Found: C, 75.2; H, 10.5; N, 3.3. $C_{27}H_{45}NO_3$ requires C, 75.1; H, 10.5; N, 3.25%). After several weeks' storage, the nitro-alcohol had become yellow and the m. p. was about 80°.

(b) The same compound was obtained (46%) by similar alkaline treatment of 6-nitrocholesterol.

(c) Sodium borohydride (37.5 mg.) in water (0.5 ml.) and dioxan (4.5 ml.) was added to a stirred solution of 6 β -nitrocholest-4-en-3-one (190 mg.) in dioxan (7.5 ml.). After 2 hr. at room temperature, addition of water, extraction with ethyl acetate, and crystallisation from aqueous methanol afforded 6 β -nitrocholest-4-en-3 β -ol (80 mg.), m. p. 150—154°. The i.r. spectrum was identical with that of the sample in (a).

6 β -Nitrocholest-4-en-3-one. Kiliani's chromic acid solution⁴ (6.98 ml.; 7.6N) was added during 2 min. to a cooled solution of the above nitrocholestenol (7.26 g.) in acetone (200 ml.), with constant swirling. After 5 min., water (400 ml.) was added and the solid product was crystallised from light petroleum (b. p. 60—80°), giving the *ketone* (6.11 g., 85%), m. p. 143—144° (from ether—light petroleum), $[\alpha]_D -103^\circ$ (*c* 2.03), $M_D -442^\circ$, $\lambda_{max.}$ (EtOH) 235 $m\mu$ (ϵ 11,600), $\nu_{max.}$ (KBr) 1690 (4-en-3-one), 1620 (C:C), 1545, 1364, and 1361 (NO_2) cm^{-1} (Found: C, 75.4; H, 10.1; N, 3.3. $C_{27}H_{43}NO_3$ requires C, 75.5; H, 10.1; N, 3.3%). In Nujol the positions of the i.r. peaks were not significantly different.

Passage of the nitro-ketone in benzene down a column of alumina (Woelm grade III, or M & B chromatographic grade) gave a little impure cholest-4-ene-3,6-dione, m. p. 115—119°, identified (mixed m. p., u.v., and i.r. spectra) by comparison with an authentic specimen.

6 α -Nitrocholest-4-en-3-one. The above 6 β -isomer (6.8 g.) was added to 0.5% methanolic potassium hydroxide (340 ml.), and the mixture was gently warmed until a clear solution was obtained. After 5 min., acetic acid was added and the solid product was crystallised from methanol, giving the *6 α -nitro-ketone* (5.11 g., 75%), m. p. 138.5—141.5° [from light petroleum (b. p. 60—80°)], $[\alpha]_D +76^\circ$ (*c* 1.95), $M_D +326^\circ$, $\lambda_{max.}$ (EtOH) 234 $m\mu$ (ϵ 14,300), $\nu_{max.}$ (KBr) 1682 (4-en-3-one) 1620 (C:C), 1546 and 1369 (NO_2) cm^{-1} (Found: C, 75.8; H, 9.9; N, 3.45%). In Nujol the positions of the peaks were not significantly different. Cholest-4-ene-3,6-dione could not be isolated after chromatography of a benzene solution of the ketone over alumina (Woelm, grade III).

Reduction of 6 α -nitrocholest-4-en-3-one. Sodium borohydride (77 mg.) in water (1 ml.) and dioxan (9 ml.) was added slowly to a stirred solution of 6 α -nitrocholest-4-en-3-one (390 mg.) in dioxan (15 ml.). After about 10 min., a solid began to separate from the yellow solution. Stirring was continued for a further 1.75 hr., an equal volume of water was added, and the solid (230 mg.) was filtered off, washed, and dried *in vacuo*. Crystallisation from methanol gave the alcohol (50 mg.) as a solid which slowly softened from 65°. Acidification of the original solution with hydrochloric acid and extraction with ethyl acetate gave more (70 mg.) of the alcohol. The combined products, considered to be 6 α -nitrocholest-4-en-3 β -ol, separated from methanol as a solid which softened to a gum from 93° and had $[\alpha]_D +28^\circ$, $\nu_{max.}$ (KBr) 3400 (OH), 1545 and 1370 (NO_2) cm^{-1} (Found: C, 74.4; H, 11.1; N, 3.4. Calc. for $C_{27}H_{45}NO_3$: C, 75.1; H, 10.5; N, 3.25%).

6-Nitrocholest-4-en-3-one pyrrolidine enamine. Treatment of either 6 α - or 6 β -nitrocholest-4-en-3-one with pyrrolidine in hot methanol afforded the same bright red *enamine*, m. p. 207—210°, $\lambda_{max.}$ (EtOH) 260 (ϵ 18,200) and 479 $m\mu$ (ϵ 29,900), $\nu_{max.}$ (KBr) 1546 (NO_2) cm^{-1} (Found:

⁴ Heusser, Roth, Rohr, and Anliker, *Helv. Chim. Acta*, 1955, **38**, 1178.

N, 5.5. $C_{31}H_{50}N_2O_2$ requires N, 5.8%). The enamine was unaffected by refluxing for 1 hr. with acetic acid-sodium acetate in aqueous methanol. It was therefore heated at 100° for 30 min. with 3N-aqueous hydrochloric acid, and the gum obtained by extraction with ether was further warmed for 10 min. with methanolic sodium hydroxide. The solution was adjusted to pH 5 with aqueous acetic acid, concentrated, and diluted with water. Repeated recrystallisation of the product from light petroleum (b. p. 40–60°) yielded 6 α -nitrocholest-4-en-3-one (19%), m. p. and mixed m. p. 132–135°.

The author thanks Mr. B. W. Sharp for technical assistance, Mr. S. Bance for the microanalyses, and Mr. T. Threlfall for the measurement of the spectra and for helpful discussions.

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549. Thermal Reactions of Cyanogen.

By C. F. CULLIS and J. G. YATES.

THE stability of cyanogen to heat is remarkable, especially in view of the highly endothermic nature of this compound. Although cyanogen does not normally suffer thermal decomposition below 1000°, polymerisation to paracyanogen takes place at much lower temperatures. A wide range of additives,¹ ultraviolet light,² a high-voltage electric discharge,³ and α -particles^{4,5} all bring about polymerisation at ambient temperatures, and paracyanogen is said to be formed in the absence of such influences when cyanogen is heated to 300–400° at atmospheric pressures, or to a lower temperature at higher pressures.^{6,7} The precise experimental conditions under which the purely thermal polymerisation takes place are, however, not well-defined, and attempts have recently been made in these laboratories to study the formation of paracyanogen from very carefully purified cyanogen.

Cyanogen was prepared by the controlled decomposition of silver cyanide *in vacuo* at 380–400°, and the resulting product was very carefully fractionated before use; gas-chromatographic analysis showed that the purified material contained no detectable impurities. The extent of polymerisation to paracyanogen was investigated by introduction of the gas at pressures up to atmospheric into a 300 cm.³ clear silica reaction vessel maintained at temperatures from 100 to 1200°. The behaviour in the region from 300 to 600° was especially carefully investigated. Under none of the conditions used, however, did appreciable reaction occur, even after periods of 14 days, as shown both by measurements of total pressure change and by periodic analysis of the contents of the reaction vessel by gas chromatography. This suggests that paracyanogen is formed only in the presence of suitable impurities and other influences which will initiate polymerisation.

However, decomposition of cyanogen to carbon and nitrogen occurs quite rapidly at higher temperatures on the surface of a heated carbon filament. The reaction-vessel assembly and the carbon filaments were the same as those used for the study of the reaction of carbon with nitrogen at sub-atmospheric pressures.⁸ The progress of the

¹ Welcher, Berets, and Sentz, *Ind. Eng. Chem.*, 1957, **49**, 1755.

² Berthelot and Gaudechon, *Compt. rend.*, 1912, **155**, 207.

³ Shekhter and Syrkina, *Compt. rend. Acad. Sci. U.R.S.S.*, 1940, **26**, 446.

⁴ Lind and Bardwell, *Science*, 1925, **62**, 593; *ibid.*, 1926, **63**, 310.

⁵ Watson, *J. Phys. Chem.*, 1947, **51**, 654.

⁶ Meyer and Goldschmidt, *Ber.*, 1882, **15**, 1164.

⁷ Briner and Wroczynski, *Compt. rend.*, 1910, **151**, 314.

⁸ Cullis and Yates, *Trans. Faraday Soc.*, 1964, **60**, 141.

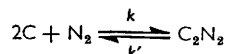
reaction could be followed either by condensation of unchanged cyanogen and measurement of the pressure of the residual nitrogen, or by determination of the increase in weight of the carbon filament.⁹ The two methods gave results in excellent agreement, but the latter method was generally more convenient. Since, during the course of a run, the layer of carbon deposited caused the electrical resistance of the filament to increase, the voltage across it was continuously adjusted to keep the filament temperature constant.

Plots of the increase in weight of the carbon filament against time show that the rate of decomposition is proportional to the initial pressure of cyanogen over the range 20—300 mm. This linear dependence of rate on cyanogen pressure is observed at all temperatures from 1600 to 2000° (see Figure), and the dependence on temperature of the first-order velocity constants (see Table) corresponds to an overall activation energy of 40.2 kcal. mole⁻¹.

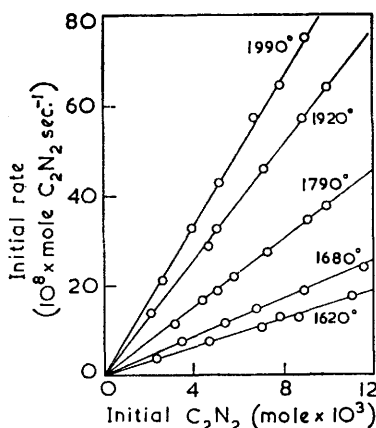
First-order velocity constants for the decomposition of cyanogen.

Temp. (°c)	1620	1680	1730	1790	1855	1920	1990
10 ⁵ k (sec. ⁻¹)	1.55	2.09	2.51	3.70	4.95	6.31	8.25

Since it has been possible to measure the velocity constants of both the forward⁸ and back reactions:



at the same temperature (2000°) and under otherwise identical experimental conditions, the equilibrium constant for the above system at 2000° can be calculated. The experimental velocity constants are, respectively, $k = 1.11 \times 10^{-7}$ sec.⁻¹, and $k' = 8.25 \times 10^{-3}$



The dependence of rate of decomposition on cyanogen pressure.

sec.⁻¹, whence $K_p = k/k' = 1.34 \times 10^{-3}$. This latter value may be compared with that derived from thermodynamic data. For the forward reaction, using standard symbols, $\Delta H_{298}^\circ = 73.8$ kcal. mole⁻¹,¹⁰ and $\Delta G_{298}^\circ = 61.7$ kcal. mole⁻¹.¹¹ Now, $C_p = 7.25 - 7.70 \times 10^{-3}T$, and hence it can readily be shown that $\Delta H_{2273}^\circ = 71.9$ kcal. mole⁻¹ and $\Delta G_{2273}^\circ = 32.3$ kcal. mole⁻¹. Substitution of the latter value into the equation, $\Delta G = -RT \ln K_p$, gives a value for K_p of 0.91×10^{-3} , which may be compared with the value of 1.34×10^{-3} deduced from kinetic data. The satisfactory agreement between the two

⁹ Cf. Palmer and Hirt, *J. Amer. Chem. Soc.*, 1962, **84**, 113.

¹⁰ Knowlton and Prosen, *J. Res. Nat. Bur. Stand.*, 1951, **46**, 489.

¹¹ Stevenson, *J. Chem. Phys.*, 1939, **7**, 171.

values indicates that the measurements of the rates of both the forward and back reactions were carried out under truly non-equilibrium conditions.

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550. *Platinum Blue and Related Complexes.*

By R. D. GILLARD and G. WILKINSON.

ONE of the first recorded reactions of a co-ordinated organic ligand was the hydrolysis of acetonitrile co-ordinated to platinum(II).¹ An analogous ammonolysis has been recently demonstrated in the formation of biacetamidinediammineplatinum(II) chloride hydrate² rather than bisacetoneitriletetra-ammineplatinum(II) chloride hydrate. The hydrolysis of dichlorobisacetoneitrileplatinum(II) is more complicated, and we report our results on this and related topics.

Platinum Blue.—The *cis*-configuration has been assigned³ to dichlorobisacetoneitrileplatinum(II) on the basis of its reactions. The infrared spectrum (solid state) agrees with *cis*-stereochemistry since there is a sharp band at 2320 cm.⁻¹ with shoulders at 2341 and 2305 cm.⁻¹; a broad band at 1024 cm.⁻¹ is due to C-N or C-C stretching. In agreement with the observation of Hofmann and Bugge,¹ the yellow dichloro-complex is converted into Platinum Blue by treatment with water and silver nitrate or sulphate; silver chloride and free acid are formed and Platinum Blue has the empirical composition Pt(MeCO·NH)₂·H₂O.

Platinum Blue is very soluble in water, methanol, and dimethylformamide from which it can be crystallised by the addition of dichloromethane. It is insoluble in ether, acetone, chloroform, benzene, and similar solvents. It is diamagnetic and, in solution in deuterium oxide, shows only one proton resonance in the region expected for methyl protons. The infrared spectrum in mulls has bands due to water (3391 and 3349), NH (3200), and CH₃ (2912 and 2862 cm.⁻¹). The spectrum at lower frequencies is obscured by the strongly hydrogen-bonded nature of the substance, although a band at 1623 cm.⁻¹ may be the carbonyl stretch, whilst other peaks occur at 1471, 1456, and 1428 cm.⁻¹, with broad bands at 1148 and 870 cm.⁻¹. The visible spectrum in water shows bands at 578, 598, 614, and 664 mμ, whose positions and intensities vary with the concentration, whilst in acid solution the bands are more intense. This behaviour is strongly reminiscent of the bisoxalato-platinum(II) system⁴ where there are bands at 420, 500, and 620 mμ. The suggestion⁴ for the bisoxalato-system that polymeric units are linked by platinum-platinum bonds is also probably most likely for Platinum Blue. In the ultraviolet region, only a rather broad absorption occurs, centred at 240 mμ, suggesting that cyclisation of the ligand to give a π-bonded "sandwich" structure as envisaged by Orgel⁵ is unlikely.

Attempts to obtain Platinum Blue by direct combination of compounds of platinum(II) with acetamide (as solid, and as silver and mercury salts) under a variety of conditions

¹ Hofmann and Bugge, *Ber.*, 1908, **41**, 312.

² Stephenson, *J. Inorg. Nuclear Chem.*, 1962, **24**, 801.

³ Lebedenskii and Golovnaya, *Izvest. Sekt. Platiny*, 1947, **20**, 84 (*Chem. Abs.*, 1950, **44**, 5309).

⁴ Korgmann and Dodel, *Proceedings 7th Int. Conf. Coord. Chem.*, Stockholm, 1962, p. 67.

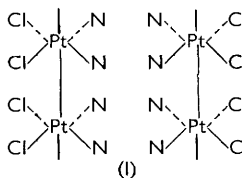
⁵ Orgel, *Chem. Soc. Special Publ.*, No. 13, 1959, p. 96.

were unsuccessful. However, the addition of potassium cyanide to solutions of Platinum Blue gave only potassium tetracyanoplatinate(II) and acetamide.

The chemical and spectroscopic evidence certainly fits best a polymeric structure involving acetamido-bridges, with the water molecules probably hydrogen-bonded within the crystal. Further, the distinct red-blue dichroism of the compound is similar to that found in bisdimethylglyoximatoplatinum and other platinum complexes where there is metal-metal interaction of units in chains.⁶ An early suggestion by Chernyaev and his co-workers⁷ involved chelate acetamido-groups, but later⁸ they suggested, although no evidence was given, that the structure was linear and contained the $\text{H}_2\text{O}-\text{Pt}-\text{Pt}-\text{OH}_2$ unit.

Other Complexes.—It has been reported⁷ that a dark compound is obtained by the interaction of *cis*-dichlorodiammineplatinum(II) tetrachloroplatinate(II) and acetamide. We have confirmed this observation but the composition of the product is variable. However, platinum-platinum bonds are probably present since all the materials we obtained gave dichroic needle crystals.

A further example is the blue compound formed by the addition of sulphuric acid to *cis*-dichlorodiammineplatinum(II).⁹ We have obtained this substance, by the original procedure, as a dark blue powder, and have obtained crystals by heating the powder in 1 : 1 sulphuric acid. Since the compound reacts when heated with water, dissolving to give a yellow solution containing 1 : 2 molar proportions of sulphuric acid and *cis*-dichlorodiammineplatinum(II), it appears that no substantial change occurs in the disposition of groups about the platinum in forming the sulphuric acid adduct. The substance is diamagnetic. The reflectance spectrum of the blue powder formed by crushing the crystals shows maxima at 550 and 635 μ , reminiscent of the absorptions of other systems where there is metal-metal interaction. The needle crystals are also very markedly dichroic, being blue-black with the electric vector parallel to the needle axis, and nearly colourless with the electric vector in the perpendicular direction. A preliminary single-crystal study by *X*-ray diffraction showed that the needle axis coincides with the unmistakable platinum-platinum vector, the distance Pt-Pt being 3.06 Å, suggesting a strong linkage. The Pt-Pt distance in Magnus's green salt, $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$, is 3.245 Å.¹⁰ The infrared spectrum suggests the presence of a symmetrical hydrogen bond, being essentially a single very broad absorption rising to 700 cm^{-1} ; the fundamental vibrations of ammonia and sulphate appear only as weak shoulders on this enormous band.



The stoichiometry, the presence of hydrogen bonding, the rather large unit-cell, and the fact that *trans*-dichlorodiammineplatinum(II) does not form such a sulphuric acid adduct led us to think that the columns of platinum atoms are in the partial environment shown in (I). The possibilities for hydrogen bonding of sulphuric acid to the co-ordinated ammonias are numerous.

Since α (*cis*)-sulphatobispyridineplatinum(II) is stated¹¹ to be almost black, we studied the effect of concentrated sulphuric acid on dichloro-2,2'-bipyridylplatinum(II). A yellow solution is formed which shows no sign of a dark adduct. After an inhibition period, probably due to the solubility of hydrogen chloride in sulphuric acid, hydrogen chloride is evolved at room temperature. Dilution of the solution precipitates yellow sulphato-2,2'-bipyridylplatinum(II). The nuclear magnetic resonance spectra of both fresh and aged solutions show no evidence for a metal-hydrogen bond.

⁶ Miller, *J.*, 1961, 4452.

⁷ Chernyaev and Nazarova, *Izvest. Sekh. Platiny*, 1951, 26, 101 (*Chem. Abs.*, 1954, 48, 13,517).

⁸ Chernyaev, Shenderetskaya, Nazarova, and Antsyshkina, ref. 4, p. 260.

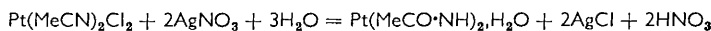
⁹ (a) Tchugaev, *J. Russ. Phys. Chem. Soc.*, 1915, 47, 213; (b) Drew, *J.*, 1934, 1790.

¹⁰ Atoji, Richardson, and Rundle, *J. Amer. Chem. Soc.*, 1957, 79, 3017.

¹¹ Gmelin-Kraut's "Handbuch der anorganischen Chemie," ed. Friedheim and Peters, Carl Winter, Heidelberg, 1915, Vol. V, Part III, p. 553.

Experimental.—Microanalyses are by the Microanalytical Laboratory, Imperial College. Infrared spectra were obtained in Nujol and hexachlorobutadiene mulls on a Perkin-Elmer model 21 spectrometer with sodium chloride or calcium fluoride optics, and on a Grubb-Parsons Spectromaster grating instrument. Electronic spectra were obtained using either the reflectance attachment to a Unicam S.P. 500 spectrophotometer, or the Perkin-Elmer model 350. Magnetic measurements were made at room temperature, using the standard Gouy method.

Dichlorobisacetoneitrileplatinum(II) and Platinum Blue. The first compound was prepared by the method of Hofmann and Bugge¹² (Found: C, 14.3; H, 1.7; N, 8.2. Calc. for $C_4H_6Cl_2N_2Pt$: C, 13.7; H, 1.7; N, 8.0%), and converted into Platinum Blue by the original method¹ (Found: C, 14.1; H, 3.2; N, 8.6; Pt, 58.9. Calc. for $C_4H_{10}N_2O_3Pt$: C, 14.6; H, 3.1; N, 8.5; Pt, 59.3%). The filtrate from the preparation was strongly acid, as required by the stoichiometry:



Dichlorobisacetoneitrileplatinum(II) (0.035 g., 10^{-4} mole) was allowed to react with a normal solution (10 ml.) of silver nitrate. After two days, the silver chloride was filtered off, and an aliquot of the blue filtrate diluted one hundred times. The pH of this solution, measured with a Cambridge pH meter, was 3.8; the theoretical pH for $2 \times 10^{-4}M$ -nitric acid is 3.699.

Interaction of Platinum Blue and cyanide. Platinum Blue (0.33 g., 10^{-3} mole) in water (5 ml.) was treated with potassium cyanide (0.26 g., 4×10^{-3} mole), giving an orange solution which was repeatedly extracted with ether. Concentration of the dried (Na_2SO_4) ether extracts gave white crystals (0.11 g., 92%), m. p. 82° (from ethanol), whose infrared spectrum was identical with that of acetamide. The aqueous phase after ether extraction was concentrated on a rotary evaporator at 30° until crystals appeared. After recrystallisation from water and drying over silica gel their infrared spectrum was identical with that of potassium tetracyanoplatinate(II) monohydrate.

Bisdichlorodiammineplatinum(II)-sulphuric acid. This, prepared by the method of Drew,^{9b} was a slimy powder (Found: Pt, 55.7. Calc. for $[Pt(NH_3)_2Cl_2]_2H_2SO_4$: Pt, 55.9%) which, on boiling with 1:1 sulphuric acid and slow cooling gave red-black needles which were collected and washed with a little ice-cold water (Found: Pt, 56.0%). Weissenberg photographs showed that the unit cell was 12.23 (needle axis) \times 12.38 \times 15.4 Å³. We have not been able to distinguish between $Z = 12$ ($\rho_{calc} = 3.41$) or $Z = 16$ ($\rho = 4.54$). The infrared spectrum showed bands at 1291 and 1143 cm^{-1} which appeared as humps on the extremely broad strong band.

Sulphato-2,2'-bipyridylplatinum(II). Dichloro-2,2'-bipyridylplatinum(II) (0.42 g., 10^{-3} mole) was treated with concentrated sulphuric acid (4 ml.); after 3 min. the initial yellow solution began to evolve hydrogen chloride. When evolution ceased the mixture was warmed to 60° for 5 min. and, after cooling, poured into water (100 ml.). The precipitated yellow compound was collected, washed with water, and dried in a vacuum (0.4 g., ca. 90%) (Found: C, 26.0; H, 1.6; N, 6.4. $C_{10}H_8N_2O_4PtS$ requires C, 26.8; H, 1.8; N, 6.3%), ν_{max} . 1605m, 1495w, 1464m, 1315m, 1269w, 1243m, 1211s, 1163s, 1129m, 1114m, 1073m, 1045s, 1028m, 1009w, 968w, 883w, 801m, 776sh, 764vs, 739m, 720s cm^{-1} . The infrared spectrum of *cis*-dichlorobipyridylplatinum(II) is extremely similar, the major difference being that the sulphato-complex shows the band at 1211 cm^{-1} due to the sulphate ligand. Minor shifts in other bands are also observed.

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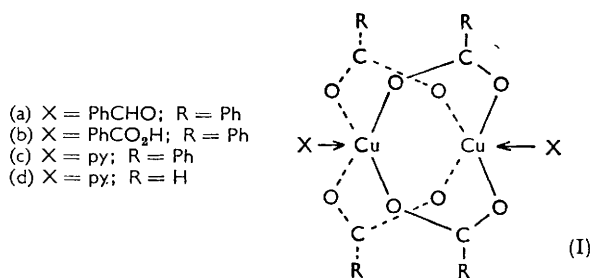
[Received, November 28th, 1963.]

¹² Hofmann and Bugge, *Ber.*, 1907, **40**, 1772.

551. Dimeric Copper(II) Carboxylates.

By R. D. GILLARD, (MISS) D. M. HARRIS, and G. WILKINSON.

A large number of adducts of copper(II) carboxylates exist, with the stoichiometry $\text{Cu}(\text{RCO}_2)_2\text{X}$, where X is a donor molecule such as water or pyridine. It is well known that many compounds of this type are magnetically non-dilute, and are better formulated as $\text{Cu}_2(\text{RCO}_2)_4\text{X}_2$, with direct contact between the copper atoms, held together by bridging carboxylate groups as in structure (I). In view of the recent disclosures of low magnetic moments for copper benzoate itself¹ and its adducts with urea² and alcohol,² we are prompted to publish our results on adducts of copper benzoate.



The reaction of copper metal with benzaldehyde in the presence of air has been known for many years. The product of the reaction was formulated³ as $\text{Cu}(\text{PhCO}_2)_2\text{PhCHO}\cdot\text{H}_2\text{O}$; we have obtained this compound by the original method, but analysis and the infrared spectrum showed the absence of water. Its magnetic moment is 1.34 B.M. per copper atom (at 293°K), strongly suggesting that it should be formulated $\text{Cu}_2(\text{PhCO}_2)_4(\text{PhCHO})_2$, with the structure (Ia). On heating under a vacuum, copper(II) benzoate and dry benzaldehyde were obtained. A very similar compound is obtained with benzoic acid itself as the addend; this has $\mu_{\text{eff}} = 1.39$ B.M., and is formulated as (Ib). It is noteworthy that the unstable compounds copper(II) acetate mono-acetaldehyde⁴ and copper(II) acetate mono-acetic acid⁵ have been reported. These are presumably dimeric, like the analogous adducts of copper(II) benzoate.

Three distinct adducts of pyridine (py) with copper(II) benzoate are reported in the literature; they are formulated^{3,6} $\text{Cu}(\text{PhCO}_2)_2\text{py}_2\cdot\text{H}_2\text{O}$ (A), $\text{Cu}(\text{PhCO}_2)_2\text{py}$ (B), and $\text{Cu}(\text{PhCO}_2)_2\text{py}_2$ (C). Compound A is magnetically normal (μ_{eff} per copper atom = 1.90 B.M.). However, B, which is obtained from A by gentle heating, has $\mu_{\text{eff}} = 1.30$ B.M., strongly indicating the dimeric structure (Ic). The magnetic moment of C is normal ($\mu_{\text{eff}} = 1.91$ B.M.).

The relationship between A and B recalls that between the adducts of pyridine with copper(II) formate, formulated⁷ as $\text{Cu}(\text{HCO}_2)_2\text{py}_2\cdot\text{H}_2\text{O}$ (D) and $\text{Cu}(\text{HCO}_2)_2\text{py}$ (E), obtained from D by gentle heating. For both the benzoate and the formate systems, the conversion is accompanied by the disappearance of the bands due to water in the infrared spectrum, and by a fall in the relative intensity of the bands due to pyridine. Whilst the magnetic moment of D is normal ($\mu_{\text{eff}} = 1.88$ B.M.), that of E is partly quenched at room

¹ Lewis and Thompson, *Nature*, 1963, **200**, 468.

² Inoue, Kishita, and Kubo, *J. Chem. Soc. Japan*, 1963, **84**, 759.

³ Briggs, Saenger, and Wardlaw, *J.*, 1931, 2552.

⁴ Davis and Green, *J. Amer. Chem. Soc.*, 1940, **62**, 1272.

⁵ Davidson and Griswold, *J. Amer. Chem. Soc.*, 1944, **66**, 1888.

⁶ King, *J.*, 1929, 2593.

⁷ King, *J.*, 1930, 2307.

temperature ($\mu_{\text{eff}} = 1.15$ B.M.), so that its structure is most likely (Id). Compound E is, in fact, the same as that studied by Martin and Waterman,⁸ who appear to have overlooked the earlier preparation.

Experimental.—Microanalyses were by the Microanalytical Laboratory, Imperial College. Infrared spectra were obtained (for mulls) using a Grubb-Parsons Spectromaster instrument. Magnetic moments (the mean of at least three determinations) were measured with a standard Gouy balance at 293°K. The known dimeric compound copper(II) acetate monopyridine⁹ (Found: C, 41.5; H, 4.3; N, 5.35. Calc. for $C_9H_{11}CuNO_4$: C, 41.4; H, 4.25; N, 5.35%) had $\mu_{\text{eff}} = 1.35$ B.M.

The page reference following each compound is to the method given in Gmelin's "Handbuch der anorganischen Chemie," Volume 60B, 1961.

Copper(II) benzoate dihydrate (p. 720) (Found: C, 49.4; H, 4.3; Cu, 18.4. Calc. for $C_{14}H_{14}CuO_6$: C, 49.2; H, 4.15; Cu, 18.6%) showed ν_{max} 3580m, 1950w, 1597s, 1550s,br, 1481w, 1411m, 1400s, 1302w, 1177w, 1063m, 1024m, 939sh, 928sh, 920s, 872s,br, 847w, 811w,br, 704s,br, 688m, and 680m cm^{-1} .

Copper(II) benzoate (p. 721) (Found: C, 54.6; H, 3.35; Cu, 20.3. Calc. for $C_{14}H_{10}CuO_4$: C, 54.95; H, 3.25; Cu, 20.8%) showed ν_{max} 1900w, 1680w, 1600s, 1555s, 1530sh, 1485w, 1400vs, 1303w, 1275w, 1173m, 1140m, 1064m, 1024s, 1000m, 974w, 931s, 860sh, 847m, 840m, 815m, 730s, 711s, 692sh, and 685s cm^{-1} .

Copper(II) benzoate benzoic acid (p. 725) (Found: C, 58.7; H, 3.65; Cu, 14.9. $C_{21}H_{16}CuO_6$ requires C, 59.0; H, 3.75; Cu, 14.8%), when heated at 80°/10 mm., gave benzoic acid as a white sublimate, m. p. 121°. No evidence was found for the 0.5H₂O given in Gmelin's "Handbuch." The compound has been reformulated recently by Japanese workers,² whose results agree with ours. They find $\mu_{\text{eff}} = 1.40$ B.M., our value being 1.39 B.M. The infrared spectrum has bands at 2620m*, 2515w*, 1675s*, 1610s, 1569s, 1490m, 1400vs, 1304m*, 1275vs, 1177m, 1160w*, 1141w, 1123m*, 1092m*, 1066m, 1024s, 1000m, 942sh*, 936sh, 929m, 857s, 845s, 836m*, 820w, 808s, 795w*, 725s, 712s, 694m, and 686s cm^{-1} . The bands marked with an asterisk disappear when the benzoic acid is removed by heating; the spectrum of the product is identical with that of copper(II) benzoate.

Copper(II) benzoate benzaldehyde, prepared by the method of Davis and Green⁴ (Found: C, 61.1; H, 4.1; Cu, 15.0. Calc. for $C_{21}H_{16}CuO_5$: C, 61.2; H, 3.9; Cu, 15.4%), showed ν_{max} 1971w, 1940w, 1911w, 1834w, 1709m*, 1686s*, 1656m*, 1613vs, 1578vs, 1495m, 1401vs, 1314m, 1281s, 1214s*, 1202sh, 1179sh, 1170m, 1127m*, 1094w, 1071m, 1023s, 1003m, 947w*, 931w, 860w, 845m, 836s*, 808m, 751s*, 743sh*, 729vs, 712vs, 692sh, and 687vs cm^{-1} . Bands marked with an asterisk disappear when the compound is heated (70°/10 mm.) to remove the benzaldehyde. The solid product is copper(II) benzoate (analysis and infrared spectrum).

An attempt was made to prepare the compound formulated^{3,4} as the monohydrate of the above. However, the product showed no infrared absorption due to water, and was extremely similar to the mono-benzaldehyde adduct (Found: C, 60.9; H, 3.65; Cu, 15.2. Calc. for the monohydrate: $C_{21}H_{18}CuO_6$: C, 58.7; H, 4.2; Cu, 15.1%).

Copper(II) benzoate bispyridine monohydrate (p. 723) (Found: C, 60.0; H, 4.45; N, 5.9. Calc. for $C_{24}H_{22}CuN_2O_5$: C, 60.0; H, 4.60; N, 5.8%) showed ν_{max} 3317m, 3237sh, 1661m, 1600s, 1559s, 1485m, 1300w, 1217m, 1165w, 1152m, 1139w, 1069s, 1042m, 1027m, 1019m, 1003w, 951w, 937m, 838w, 823w, 756s, 716s, 698s, and 679s cm^{-1} .

Copper(II) benzoate bispyridine (p. 723) (Found: C, 62.6; H, 4.85; N, 6.2. Calc. for $C_{24}H_{20}CuN_2O_4$: C, 62.1; H, 4.35; N, 6.05%) showed ν_{max} 1602m, 1557s, 1486m, 1302w, 1216m, 1167w, 1151m, 1069s, 1043m, 1028m, 1018m, 1001w, 938m, 837w, 757m, 716s, 697s, and 681s cm^{-1} . For this compound to be obtained without contamination by its monohydrate, both the copper benzoate and the pyridine used in its preparation must be anhydrous.

Copper(II) benzoate monopyridine (p. 723) (Found: C, 59.2; H, 3.65; N, 3.7. Calc. for $C_{15}H_{15}CuNO_4$: C, 59.3; H, 3.9; N, 3.65%) showed ν_{max} 1629s, 1599m, 1567s, 1487w, 1400s, 1219m, 1173w, 1159sh, 1150m, 1068m, 1038m, 1026m, 1012m, 975w, 942w, 846m, 819w, 761m, 756sh, 730sh, 723s, 718sh, 707m, 701m, 695m, and 686s cm^{-1} .

⁸ Martin and Waterman, *J.*, 1959, 2960.

⁹ Hanicova, Hanic, and Stempelova, Abstracts of the 7th Internat. Conf. on Coord. Chem., Stockholm, 1962, p. 79.

Copper(II) formate bispyridine monohydrate, prepared according to King ⁷ (Found: C, 43.35; H, 4.25; N, 8.5. Calc. for C₁₂H₁₄CuN₂O₅: C, 43.65; H, 4.3; N, 8.5%), showed ν_{\max} 3496s, 3460sh, 3070vw, 2865w, 2110w,br, 1966w,br, 1875w,br, 1592s,br, 1487w, 1453s, 1379s, 1328s, 1241w, 1222s, 1162m, 1074s, 1046s, 1017s, 785m, 764s, and 696s cm⁻¹.

Copper(II) formate monopyridine. The previous compound was kept at 55°/10 mm. until no further change in weight occurred (weight loss from the product is very slow indeed under these conditions), giving a product (Found: C, 36.15; H, 2.95; N, 5.8. Calc. for C₇H₇CuNO₄: C, 36.1; H, 3.05; N, 6.0%), m. p. 144° (lit.,⁸ 144°), ν_{\max} 2860w, 1640s, 1615m, 1601sh, 1450m, 1379m, 1369m, 1350s, 1221s, 1162m, 1069m, 1037s, 1008m, 775s, 757s, and 696s cm⁻¹.

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552. Ultraviolet Spectra of the Alkyl Cyanide Complexes of Titanium(IV) and Zirconium(IV) Halides.

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THE preparation ¹ and infrared spectra ² of the 1 : 2 adducts (MX₄.2RCN) formed by titanium(IV) and zirconium(IV) halides with alkyl cyanides are well described in the literature. The stereochemistry of these complexes is still in doubt, although Ulich *et al.*³ consider the adduct TiCl₄.2EtCN to be *cis* on the basis of dipole moment measurements. Also, the infrared spectra of several of these complexes have been measured in the caesium bromide region, and appear to suggest a *cis*-configuration.⁴

The complexes TiCl₄.2MeCN and ZrBr₄.2MeCN behave as non-electrolytes when dissolved in methyl cyanide, the solutions having molar conductivities of 2.7 and 8.2 ohm⁻¹ cm.², respectively, at 25°; Et₄NBr, a typical 1 : 1 electrolyte, has a molar conductivity of 159 ohm⁻¹ cm.² in methyl cyanide.

We have measured the ultraviolet spectra of the methyl and ethyl cyanide adducts of titanium and zirconium tetrachlorides and tetrabromides in the appropriate cyanide (see Table). Since the quadrivalent metals have *d*⁰ configurations, transitions of the *n* → π^*

Absorption spectra (cm.⁻¹) of MX₄.2RCN complexes.*

Complex	Band 1	Band 2	Band 3	Complex	Band 1	Band 2	Band 3
TiCl ₄ .2MeCN	45,050	31,750	—	ZrCl ₄ .2MeCN	45,660	34,480	27,780
TiCl ₄ .2EtCN	44,050	31,650	—	ZrCl ₄ .2EtCN	44,250	33,670	27,400
TiBr ₄ .2MeCN	36,630	25,000	—	ZrBr ₄ .2MeCN †	37,740	25,510	21,410
TiBr ₄ .2EtCN	35,970	24,810	—	ZrBr ₄ .2EtCN †	38,460 †	25,380	20,620

* Measurements in EtCN were not reliable above 46,000 cm.⁻¹ because of absorption by the solvent.

† Shoulders at 40,100 and 36,200 cm.⁻¹.

‡ Further absorption peak at 47,390 cm.⁻¹.

¹ Emeléus and Rao, *J.*, 1958, 4245.

² Coerver and Curran, *J. Amer. Chem. Soc.*, 1958, 80, 3522.

³ Ulich, Hertel, and Nespital, *Z. phys. Chem.*, 1932, 17b, 21.

⁴ Beattie, personal communication.

type, as observed for $\text{TiCl}_3 \cdot 3\text{MeCN}$,⁵ cannot occur. All the peaks have extinction coefficients greater than 1000, and must be associated with the transfer of charge from the ligand π -orbitals to the metal d -levels.

The spectrum of the hexachlorotitanate(IV) anion in 12M-hydrochloric acid has one peak, at $45,000 \text{ cm}^{-1}$, which has been assigned to a $\text{Cl}(\pi) \rightarrow \gamma_5$ transition.⁶ An analogous peak at $46,000 \text{ cm}^{-1}$ is observed⁷ for the $[\text{ZrCl}_6]^{2-}$ anion; the small blue shift agrees with the chemical fact that it is harder to reduce zirconium than titanium. Bands occurring in the $45,000 \text{ cm}^{-1}$ region for the alkyl cyanide complexes of the tetrachlorides (band 1) are accordingly attributed to $\text{Cl}(\pi) \rightarrow \gamma_5$ transitions. (These complexes have lower symmetry than O_h , so γ_3 and γ_5 are intended to be general descriptions.) A comparison of the band 1 peaks for corresponding chloride and bromide complexes shows a large red shift from chloride to bromide; a similar shift is observed for the tetrahalides themselves. Band 1 in the bromide complexes is presumably associated with the $\text{Br}(\pi) \rightarrow \gamma_5$ transition, and the red shift shows that it is much easier to transfer the π -electrons of bromine than those of chlorine. $\text{ZrBr}_4 \cdot 2\text{MeCN}$ shows an additional peak of very high extinction coefficient at $47,390 \text{ cm}^{-1}$ which is not found for the other complexes. This may result from a $\text{Br}(\pi) \rightarrow \gamma_3$ transition.

The peaks observed at lower wave-number (*i.e.*, band 2) are likely to result from the transfer of the alkyl cyanide π -electrons to the non-bonding γ_5 metal orbitals, *i.e.*, an $\text{RCN}(\pi) \rightarrow \gamma_5$ transition. The zirconium complexes show two such peaks, however (*i.e.*, band 3 as well), but the cause of this splitting is as yet unknown.

Transitions of the type $\sigma \rightarrow \gamma_3$, which are often observed⁸ in the hexahalide complexes of the transition metals, are not found in the alkyl cyanide complexes, and presumably occur at higher wave-numbers (beyond the range of our measurements).

Experimental.—All manipulations were carried out in the usual closed vacuum system.

The complexes were prepared² by sealing into ampoules the halide with excess of alkyl cyanide. The ampoules were opened when required, and removal of excess cyanide left the crystalline complexes. The alkyl cyanides were dried by repeated distillation *in vacuo* from phosphoric oxide.

Ultraviolet spectra were measured in "spectragrade" alkyl cyanide, using 1-cm. silica cells and an S.P. 700 spectrophotometer (Unicam). The solutions were made up under a vacuum, and the cells removed from the vacuum system by use of an adaptor which ensured that the vacuum was maintained during the measurements.

Conductivity measurements were carried out in specially adapted cells, with a Phillips PR 9500 bridge.

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⁵ Duckworth, Fowles, and Hoodless, *J.*, 1963, 5665.

⁶ Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, London, 1962, p. 284.

⁷ Drake and Fowles, *J. Inorg. Nuclear Chem.*, 1961, **18**, 136.

⁸ Jørgensen, *Mol. Phys.*, 1959, **2**, 309.

553. Reactions of Niobium(v) and Tantalum(v) Chlorides and Bromides with Alkyl Cyanides.

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RECENTLY, the reactions of alkyl cyanides with halides of the titanium, vanadium, and chromium sub-group metals have been examined in some detail. The tetrahalides of titanium and zirconium form 1 : 2 adducts,¹ and consideration of their infrared² spectra suggests that these have a *cis*-configuration. The vanadium(IV) analogues^{3,4} are readily reduced by excess of alkyl cyanide to give the trivalent adducts $VCl_3 \cdot 3RCN$; similarly, molybdenum(V) chloride, tungsten(VI) chloride, and tungsten(V) chloride and bromide are reduced to give complexes $MX_4 \cdot 2RCN$,⁵ which contain the metal in the M^{+4} oxidation state.

In this Paper we report the reactions of the chlorides and bromides of quinquivalent niobium and tantalum. All four halides readily dissolve in excess of alkyl cyanide, RCN ($R = Me, Et, \text{ and } Pr^n$), and removal of the excess solvent results in the deposition of crystalline 1 : 1 adducts (see Table) which are diamagnetic and thus contain quin-

Analytical data for the $MX_5 \cdot RCN$ complexes.

Compound	Found (%)			Calc. (%)			Colour	Mol. wt.*		Λ_m ($ohm^{-1} cm.^2$)
	M	X	N	M	X	N		Found	Calc.	
$NbCl_5 \cdot MeCN$	29.1	56.5	4.6	29.9	57.0	4.5	Yellow	368	311	—
$NbCl_5 \cdot EtCN$	27.6	54.0	4.0	28.6	54.5	4.3	Yellow	325	325	4.0
$NbCl_5 \cdot Pr^nCN$	26.6	51.2	4.2	27.4	52.3	4.1	Yellow	340	339	—
$NbBr_5 \cdot MeCN$	17.7	75.2	2.4	17.4	74.9	2.6	Dark red	—	—	—
$NbBr_5 \cdot EtCN$	16.9	72.5	—	17.0	73.0	2.6	Dark red	572	548	8.0
$NbBr_5 \cdot Pr^nCN$	16.3	70.5	2.4	16.5	71.15	2.5	Dark red	—	—	—
$TaCl_5 \cdot MeCN$	45.7	43.9	3.4	45.3	44.4	3.5	White	407	399	—
$TaCl_5 \cdot EtCN$	44.1	42.2	3.4	43.8	42.9	3.4	White	482	413	3.0
$TaCl_5 \cdot Pr^nCN$	43.3	41.0	3.1	42.3	41.5	3.3	White	477	428	—
$TaBr_5 \cdot MeCN$	29.6	64.3	2.3	29.1	64.3	2.3	Yellow	—	—	2.0
$TaBr_5 \cdot EtCN$	29.0	62.7	2.2	28.5	62.9	2.2	Yellow	640	636	23.0
$TaBr_5 \cdot Pr^nCN$	28.4	60.7	2.3	27.8	61.5	2.2	Yellow	677	650	—

* Measured in benzene solution; calculated values are for monomers. † Measured in RCN solution at *ca.* $10^{-3}M$ concentration.

quevalent niobium and tantalum. Conductance measurements on solutions of a selection of the adducts in excess of alkyl cyanide show that they are non-electrolytes. For all compounds examined, except one (cf. Table), Λ_m values of $8 ohm^{-1} cm.^2$ or less were obtained, in contrast to values of $150-160 ohm^{-1} cm.^2$ found for typical 1 : 1 electrolytes in these solvents.⁴ Ebullioscopic measurements on benzene solutions of nine of the compounds showed that they are monomeric. Monomeric compounds of this type have not previously been reported, although the pentahalides form 1 : 1 adducts with diethyl ether that are monomeric in diethyl ether solution;⁶ in such solutions the lowering of

¹ Emeléus and Rao, *J.*, 1958, 4245.

² Beattie, personal communication.

³ Funk, Mohanpt, and Paul, *Z. anorg. Chem.*, 1959, 302, 199.

⁴ Duckworth, Fowles, and Hoodless, *J.*, 1963, 5665.

⁵ Allen, Brisdon, and Fowles, *J.*, 1964, in the press.

⁶ Cowley, Fairbrother, and Scott, *J.*, 1958, 3133.

vapour pressure indicated that there was additional co-ordination of ether molecules at 0°. Dialkyl sulphides also give 1:1 adducts $\text{MX}_5\cdot\text{SR}_2$ with the pentahalides, but no molecular weight data are available.⁷

The infrared spectra of the $\text{MX}_5\cdot\text{RCN}$ complexes show the usual increase in the $\nu(\text{C}\equiv\text{N})$ frequency, this increase being 30–50 cm^{-1} over the twelve compounds. Metal-halogen (other than fluoride) stretching frequencies occur below 400 cm^{-1} for octahedral complexes [$(\text{NbCl}_5)_2$ has peaks at 397s and 363w²], and were not, therefore, detected.

Since molybdenum(v) chloride and the halides of quinque- and sexi-valent tungsten are reduced to the quadrivalent state by excess of alkyl cyanide, it seemed possible that the niobium(v) and tantalum(v) halides might also undergo reduction, particularly at higher temperatures. We found no reduction, however, even on prolonged periods of reflux or reaction in a sealed tube at 150°, although there was a darkening of the solution; this might have resulted from a breakdown of the alkyl cyanide. The compounds we had hoped to obtain, $\text{MX}_4\cdot 2\text{RCN}$, have now been prepared⁸ by the direct reaction of the tetrahalides with alkyl cyanides.

The solutions formed by the pentachlorides in the alkyl cyanides are useful as starting materials for the preparation of complexes of niobium and tantalum in both the quinque- and quadri-valent states. It has been shown recently,⁹ for instance, that, when bipyridyl or 1,10-phenanthroline is added to such solutions, reduction takes place quite readily, and adducts of the type $\text{MCl}_4\cdot\text{B}$ (B = bipyridyl and 1,10-phenanthroline) are formed.

Experimental.—The halides of niobium and tantalum were prepared from the powdered metals as described previously.¹⁰ The alkyl cyanides, which were of the highest grade available, were finally dried by repeated distillation *in vacuo* from phosphoric oxide.

Chlorine and bromine were determined gravimetrically as the silver halides; niobium and tantalum were determined by precipitation of the hydrated oxide by addition of ammonium hydroxide, followed by ignition to the oxide.

Since the halides and the complexes formed by them are extremely sensitive to moisture, all handling procedures involved an all-glass closed vacuum system. The halides dissolved readily in alkyl cyanide, and removal of excess solvent resulted in the deposition of the crystalline 1:1 adducts. Any loosely-held alkyl cyanide was removed *in vacuo* (10 hr.).

Infrared spectra were measured for Nujol mulls on Unicam S.P. 100 and 200 spectrophotometers. A Phillips Conductivity Bridge (PR 9500) and a specially modified conductivity cell were used for the measurement of the conductivity of solutions of the complexes in the appropriate alkyl cyanide. Molecular weight determinations were carried out ebullioscopically on benzene solutions.

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⁷ Fairbrother and Nixon, *J.*, 1962, 150.

⁸ McCarley, personal communication.

⁹ Allbutt, Feenan, and Fowles, *J. Less-Common Metals*, 1964, **6**, 299.

¹⁰ Carnell and Fowles, *J.*, 1959, 4113; *J. Less-Common Metals*, 1962, **4**, 40.

554. 1-Benzyl-3-methylnaphthalene from Benzyl Methyl Ketone.

By L. A. CORT, R. G. MANDERS, and G. R. PARLETT.

IN 1897 Goldschmiedt and Knöpfer reported ^{1a} a reaction between benzyl methyl ketone, benzaldehyde, and concentrated sulphuric acid in acetic acid, leading to a compound first thought to be a dehydration trimer of the ketone but shown subsequently ^{1b} to be stilbene.

In the present work benzyl methyl ketone was boiled with 70% sulphuric acid, to yield, on distillation, a fraction from which separated a hydrocarbon, C₁₈H₁₆. Although self-condensation of the ketone under acid conditions would be expected ² initially to involve the methylene rather than the methyl group, the ¹H resonance spectrum of the product (Table) is consistent with its formulation as 1-benzyl-3-methylnaphthalene and not 1,3-dimethyl-2-phenylnaphthalene.

Experimental.—Benzyl methyl ketone (50 g.) was boiled with an equal volume of 70% sulphuric acid (w/v) for 15 min. The cold diluted mixture was extracted with benzene, to yield recovered ketone (14 g.), b. p. 75—80°/5.0 mm., a yellow oil (15 g.), b. p. 145—155°/0.4 mm., and a residue (7 g.) which did not distil at 200°/0.4 mm. After 18 months the yellow oil had deposited crystals (7.8 g.) of 1-benzyl-3-methylnaphthalene which separated from ethanol-water as rhombs, m. p. 58—59° (Found: C, 93.0; H, 6.9. C₁₈H₁₆ requires C, 93.1; H, 6.9%). The 1,3,5-trinitrobenzene *addition compound* formed yellow needles, m. p. 118° (from benzene) (Found: C, 64.6; H, 4.2; N, 9.4. C₂₄H₁₆N₃O₆ requires C, 64.7; H, 4.3; N, 9.4%). The *picrate* formed orange-yellow needles, m. p. 94—94.5° (from benzene) (Found: C, 62.6; H, 4.1; N, 9.0%; Equiv., 479. C₂₄H₁₆N₃O₇ requires C, 62.5; H, 4.15; N, 9.1%; Equiv., 461).

The residue above yielded no crystalline picrate, and no evidence was obtained for the presence of a trimer (analogous to mesitylene formation from acetone). The yield of hydrocarbon was considerably lowered by cutting the time of reaction to 5 min. or less, by using 40% sulphuric acid, and by using polyphosphoric acid.³

Assignments for ¹H resonance spectra at 60 Mc/sec., in carbon tetrachloride.

1-Benzyl-naphthalene.*				1-Benzyl-3-methylnaphthalene.			
Band	τ	Rel. intensity	Assignment	Band	τ	Rel. intensity	Assignment
1	2.3—2.8		Aryl H	1	2.5—3.0		Aryl H
	2.71	~5	Phenyl H		2.84	~5	Phenyl H
2	5.62	2	CH ₂	2	5.68	2	CH ₂
				3	7.59	3	CH ₃

* Dziewonski and Dziecielewski, *Bull. internat. Acad. polon.*, 1927, A, 273.

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¹ Goldschmiedt and Knöpfer, *Monatsh.*, (a) 1897, **18**, 437; (b) 1898, **19**, 406.

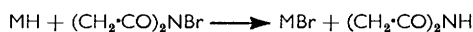
² Noyce and Snyder, *J. Amer. Chem. Soc.*, 1958, **80**, 4033, and references therein.

³ Arcus and Barrett, *J.*, 1958, 2740.

555. Reactions of *N*-Bromosuccinimide with Inorganic Hydrides.

By W. GEE, R. A. SHAW, and B. C. SMITH.

N-HALOGENOSUCCINIMIDES and related organic *N*-halogeno-imides are well-known halogenating, oxidising, and dehydrogenating agents in organic chemistry.^{1,2} A survey of inorganic systems suggests that, although reactions of chloramine are under extensive investigation,^{2,3} there are few reported reactions of *N*-bromosuccinimide. These include the bromination of dialkyl or diaryl phosphonates (phosphites), (RO)₂POH, to give bromophosphonates, (RO)₂P(O)Br,⁴ the dearylation of tetraphenyltin,⁵ and the formation of an addition compound with triphenylphosphine.¹ The use of *N*-bromosuccinimide as a brominating agent for organic compounds depends on the presence of an active hydrogen atom attached to carbon. Most inorganic hydrides have fairly reactive element-hydrogen bonds, and the use of *N*-halogenosuccinimides in the halogenation of inorganic hydrides has wide application.



Examples of the use of *N*-bromosuccinimide in the bromination of hydrides of non-metals are reported here. The reactions are carried out conveniently in carbon tetrachloride. *N*-Bromosuccinimide sinks to the bottom but succinimide floats on the surface as soon as it is formed, and this enables the course of the reaction to be readily followed.

Substitution of the hydrogen atoms in triphenylsilane and triethylgermane gives triphenylbromosilane and triethylbromogermane, respectively. Partial substitution of the hydrogen atoms in phenylsilane, PhSiH₃, to give, for example, phenylbromosilane, PhSiH₂Br, is readily achieved by use of one equivalent of *N*-bromosuccinimide. Reaction of the product with an excess of methylmagnesium iodide gives methylphenylsilane, MePhSiH₂. Silicon-hydrogen bonds do not react with Grignard reagents under these conditions. The reaction of *N*-bromosuccinimide with diphenylphosphine, to give diphenylbromophosphine, is particularly valuable since the bromination proceeds smoothly without further oxidation, even in the presence of an excess of *N*-bromosuccinimide.

The use of *N*-halogenosuccinimides in the halogenation of inorganic hydrides offers a number of distinct advantages over the more conventional halogenating agents; stoichiometric quantities are easily measured, and partial substitution is accomplished readily. Hydrogen halides are not formed, and hence the presence of a base as hydrogen halide acceptor is not required; these are valuable attributes when compounds sensitive to acid and/or alkali are to be halogenated. Lower valency states can be halogenated without oxidation, and side-reactions have not been observed in the course of the present work.

Experimental.—*Phenylsilane.* *N*-Bromosuccinimide (16.5 g., 0.09 mole) reacted vigorously with phenylsilane (10.0 g., 0.09 mole) in carbon tetrachloride. The mixture was boiled under reflux (1 hr.), the solvent removed by fractional distillation, and the residue extracted with ether (200 ml.). The ether solution was filtered in an atmosphere of nitrogen and allowed to react with the Grignard reagent prepared from magnesium (4.8 g., 0.2 mole) and methyl iodide (28.4 g., 0.2 mole) in ether. The mixture was heated under reflux (1 hr.) and hydrolysed with 2*N*-hydrochloric acid (200 ml.). The ether layer was separated, washed with water, 5% sodium hydrogen carbonate solution, and water, dried (Na₂SO₄), and filtered. Fractional distillation gave methylphenylsilane (6.0 g., 53%), b. p. 134—137°, *n*_D²⁵ 1.499 (lit.,⁶ 1.505) (Found: C, 69.4; H, 8.5. Calc. for C₇H₁₀Si: C, 68.8; H, 8.25%).

¹ Horner and Winkelmann, *Angew. Chem.*, 1959, **71**, 349.

² Filler, *Chem. Rev.*, 1963, **63**, 21.

³ See, e.g., Sisler, Sarkis, Ahuja, Drago, and Smith, *J. Amer. Chem. Soc.*, 1959, **81**, 2982; Sisler, Ahuja, and Smith, *J. Amer. Chem. Soc.*, 1961, **83**, 1819.

⁴ Kenner, Todd, and Weymouth, *J.*, 1952, 3675; Goldwhite and Saunders, *J.*, 1955, 3564.

⁵ Kupchik and Lanigan, *J. Org. Chem.*, 1962, **27**, 3661.

⁶ Harvey, Nebergall, and Peake, *J. Amer. Chem. Soc.*, 1954, **76**, 4555.

Triphenylsilane. *N*-Bromosuccinimide (3.7 g., 0.02 mole) was heated for 1 hr. with triphenylsilane (5.4 g., 0.02 mole) in boiling carbon tetrachloride. Succinimide was filtered off from the cooled solution in an atmosphere of nitrogen, and the solvent was removed by flash-distillation. The solid residue was sublimed in a vacuum, to give colourless crystalline triphenylbromosilane (5.6 g., 80%), m. p. 120° (lit.,⁷ 120—121°) (Found: Br, 42.5. Calc. for C₁₈H₁₅BrSi: Br, 42.4%).

Triethylgermane. Similar reaction of *N*-bromosuccinimide (5.3 g., 0.03 mole) with triethylgermane (4.7 g., 0.03 mole), and distillation of the liquid residue, gave triethylbromogermane (5.8 g., 83%), b. p. 188—191° (lit.,⁸ 190.9°) (Found: Br, 32.8. Calc. for C₁₈H₁₅BrGe: Br, 33.3%).

Diphenylphosphine. Similar reaction of *N*-bromosuccinimide (7.75 g., 0.044 mole) with diphenylphosphine (8.1 g., 0.044 mole), and distillation of the liquid residue, gave diphenylbromophosphine (5.5 g., 52%), b. p. 154°/2.5 mm. (lit.,⁹ 179—180°/12 mm.) (Found: Br, 31.95. Calc. for C₁₂H₁₀BrP: Br, 32.1%).

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⁷ McCusker and Reilly, *J. Amer. Chem. Soc.*, 1953, **75**, 1583.

⁸ Kraus and Flood, *J. Amer. Chem. Soc.*, 1932, **54**, 1635.

⁹ Petrov, Smirnov, and Emel'yanov, *Zhur. obshchei Khim.*, 1961, **31**, 3027.

556. *The cis-Forms of 2-Methoxycyclohexanol and 2-Methoxycyclopentanol.*

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THE *trans*-forms of 2-methoxy-cyclohexanol and -cyclopentanol are readily available by methanolysis of the appropriate epoxides,^{1,2} but the pure *cis*-isomers are apparently unknown. A method which separated *cis-trans*-mixtures of 3- or 4-methoxycyclohexanol³ failed with the 2-substituted compounds. We have applied the benzoate exchange reaction⁴ to prepare stereochemically pure *cis*-2-methoxy-cyclohexanol and -cyclopentanol.

Treatment of *trans*-2-methoxycyclohexyl methanesulphonate with sodium benzoate in boiling dimethylformamide resulted in smooth conversion into the *cis*-benzoate and thence into *cis*-2-methoxycyclohexanol by saponification. Similarly, *trans*-2-methoxycyclopentanol was converted into the *cis*-isomer. All the methoxy-alcohols were characterised as the *p*-phenylazobenzoates.⁵

The following data confirmed the structures and configurations of the *cis*-methoxy-alcohols. The infrared spectra⁴ in the OH stretching region for *ca.* 0.005M-solutions in carbon tetrachloride showed the following absorptions for free and intramolecularly bonded hydroxyl groups:^{4,6} *trans*-2-methoxycyclohexanol, bonded OH at 3594 cm.⁻¹ ($\Delta\nu$ 35 based on absorption for free secondary hydroxyl groups⁷ at 3629 cm.⁻¹); *cis*-isomer, bonded OH at 3586 cm.⁻¹ ($\Delta\nu$ 43). A parallel is provided by the $\Delta\nu$ values of 27 and 42 for cyclohexane-*trans*- and -*cis*-1,2-diol.⁸ The $\Delta\nu$ values, which reflect⁶ the length of

¹ Mousseron, Grangeret, and Merle, *Bull. Soc. chim. France*, 1947, 459.

² Winstein and Henderson, *J. Amer. Chem. Soc.*, 1943, **65**, 2196.

³ Eliel and Brett, *J. Org. Chem.*, 1963, **28**, 1923.

⁴ Foster, Harrison, Lehmann, and Webber, *J.*, 1963, 4471, and references therein.

⁵ Baggett, Foster, Haines, and Stacey, *J.*, 1960, 3528.

⁶ Kuhn, *J. Amer. Chem. Soc.*, 1952, **74**, 2492; 1954, **76**, 4323.

⁷ Cole and Jefferies, *J.*, 1956, 4391.

⁸ Spedding, *J.*, 1961, 3617.

intramolecular hydrogen bonds, indicate more facile bonding in the *cis*-isomers. *trans*-2-Methoxycyclopentanol showed absorption for free OH at 3627 cm^{-1} (cf. cyclopentane-*trans*-1,2-diol, 3620 cm^{-1}), and the *cis*-isomer showed absorption for bonded OH at 3570 cm^{-1} ($\Delta\nu$ 57, cf. $\Delta\nu$ 61 for cyclopentane-*cis*-1,2-diol⁶).

The nuclear magnetic resonance spectrum (determined with a Varian A60 spectrometer, with tetramethylsilane as external reference) of a chloroform solution containing 5% of *cis*-2-methoxycyclopentanol and 10% of the *trans*-isomer had, *inter alia*, signals for the methoxyl protons at δ 3.31 and 3.27, of relative strengths 1 : 2; the displacement to lower field of the signal in the *cis*-isomer is clearly due to the proximity of the hydroxyl group.

Each of the four methoxy-alcohols was smoothly demethylated with boron trichloride,⁹ to give a stereochemically pure diol with unchanged configuration. The diols were crystalline in the cyclohexane series and liquids in the cyclopentane series, the latter being characterised as the *p*-phenylazobenzoates.

The benzoate exchange reaction is potentially of wide application in the alicyclic and other series for the preparation of pure epimeric alcohols provided that one stereochemically pure alcohol is available.

Experimental.—*Conversion of trans-2-methoxycyclohexanol into the cis-isomer.* *trans*-2-Methoxycyclohexanol^{1,2} had b. p. 184°/760 mm., n_D^{25} 1.4534, and gave⁵ a *p*-phenylazobenzoate, m. p. 57—58° (from aqueous ethanol) (Found: C, 71.15; H, 6.4; N, 8.55. $\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_3$ requires C, 71.0; H, 6.55; N, 8.3%).

A cooled (0°) solution of *trans*-2-methoxycyclohexanol (4.8 g.) in dry pyridine (10 ml.) was treated dropwise with methanesulphonyl chloride (7.5 ml.). After storage at room temperature for 3 hr., the mixture was treated with water (2 ml.), and after 30 min. it was poured into ice-water (500 ml.). The mixture was extracted with chloroform (3 × 50 ml.), and the combined extracts were washed with water, ice-cold 0.1N-hydrochloric acid, and water, dried (MgSO_4), and concentrated. Distillation of the residue gave *trans*-2-methoxycyclohexyl methanesulphonate (4.3 g., 60%), b. p. 136°/0.1 mm. (Found: C, 46.2; H, 7.6; S, 15.7. $\text{C}_8\text{H}_{16}\text{O}_4\text{S}$ requires C, 46.1; H, 7.7; S, 15.4%).

A solution of the methanesulphonate (4.3 g.) in dimethylformamide (188 ml.) was boiled in the presence of sodium benzoate (15.4 g.) for 6 hr. The cooled mixture was diluted with water (100 ml.) and extracted with chloroform (150 ml.). The extract was washed with aqueous sodium hydrogen carbonate and water, dried (MgSO_4), and concentrated. Distillation of the residue gave *cis*-2-methoxycyclohexyl benzoate (4.2 g., 60%), b. p. 126°/0.5 mm. (Found: C, 71.5; H, 7.7. $\text{C}_{14}\text{H}_{18}\text{O}_3$ requires C, 71.8; H, 7.7%).

The foregoing benzoate (4 g.) was treated with a boiling solution of sodium hydroxide (10.4 g.) in water (48 ml.) and methanol (32 ml.) for 5 hr. The hydrolysate was extracted with chloroform (3 × 100 ml.), and the combined extracts were washed with water, dried (MgSO_4), and concentrated. Distillation of the residue gave *cis*-2-methoxycyclohexanol (1 g., 45%), b. p. 75°/20 mm. (Found: C, 64.4; H, 10.6. $\text{C}_7\text{H}_{14}\text{O}_2$ requires C, 64.6; H, 10.8%). The *p*-phenylazobenzoate, prepared in the usual way,⁵ had m. p. 54—55° [from light petroleum (b. p. 60—80°)] (Found: C, 70.7; H, 6.85; N, 8.5. $\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_3$ requires C, 71.0; H, 6.55; N, 8.3%).

cis-2-Methoxycyclopentanol. Using essentially the same conditions as those described above, *trans*-2-methoxycyclopentanol¹ was converted into the following derivatives: *trans*-2-methoxycyclopentyl *p*-phenylazobenzoate, m. p. 68—69° (from aqueous ethanol) (Found: C, 69.9; H, 6.4; N, 8.6. $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_3$ requires C, 70.35; H, 6.2; N, 8.6%); *trans*-2-methoxycyclopentyl methanesulphonate (50%), b. p. 116°/0.1 mm. (Found: C, 43.2; H, 7.5; S, 16.9. $\text{C}_7\text{H}_{14}\text{O}_4\text{S}$ requires C, 43.3; H, 7.3; S, 16.5%); *cis*-2-methoxycyclopentyl benzoate (67%), b. p. 118°/1.0 mm. (Found: C, 70.9; H, 7.2. $\text{C}_{13}\text{H}_{16}\text{O}_3$ requires C, 70.9; H, 7.3%); *cis*-2-methoxycyclopentanol (51%), b. p. 52°/20 mm. (Found: C, 62.1; H, 10.5. $\text{C}_6\text{H}_{12}\text{O}_2$ requires C, 62.0; H, 10.4%); *cis*-2-methoxycyclopentyl *p*-phenylazobenzoate, m. p. 36—37° [from light petroleum (b. p. 40—60°)] (Found: C, 71.0; H, 6.3; N, 8.6. $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_3$ requires C, 70.35; H, 6.2; N, 8.6%).

Demethylation experiments. A solution of *trans*-2-methoxycyclohexanol (1 g.) in dichloromethane (10 ml.) at -80° was treated with boron trichloride (7 ml.). The mixture was allowed to attain room temperature and, after 2 hr., evaporated to dryness at *ca.* 20°/12 mm. Methanol

* Bonner, Bourne, and McNally, *J.*, 1960, 2929.

was repeatedly distilled from the residue, which was then recrystallised from ethyl acetate, to give cyclohexane-*trans*-1,2-diol (0.7 g., 78%), m. p. and mixed m. p. 102—103°. Examination of the crude product by thin-layer chromatography on Kieselgel, using benzene-ethanol (4 : 1) and detection with vanillin-sulphuric acid¹⁰ or iodine vapour, revealed the absence of methoxy-compound, and examination by ionophoresis using the enclosed-strip technique¹¹ and a borate buffer (pH 10), and detection with ammoniacal silver nitrate, revealed the absence of *cis*-diol (M_G value¹² 0.07); the *trans*-diol has M_G 0.00.

Under essentially similar conditions, *cis*-2-methoxycyclohexanol was converted into cyclohexane-*cis*-1,2-diol, m. p. and mixed m. p. 96° (from ethyl acetate); the purity of the crude product was established as for the *trans*-isomer above.

In the cyclopentane series, the *trans*-methoxy-alcohol gave the *trans*-diol with R_F 0.53 in thin-layer chromatography on Kieselgel using benzene-methanol (4 : 1) and M_G 0.00, which was characterised as the *di*-*p*-phenylazobenzoate, m. p. 174—175° [from benzene-light petroleum (b. p. 60—80°)] (Found: C, 71.7; H, 5.0; N, 11.15. $C_{31}H_{26}N_4O_4$ requires C, 71.8; H, 5.05; N, 10.8%). The *cis*-methoxy-alcohol gave the *cis*-1,2-diol with R_F 0.42 and M_G 0.69; the *di*-*p*-phenylazobenzoate had m. p. 156° (Found: C, 71.3; H, 5.1; N, 10.9%).

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¹⁰ "Chromatography," E. Merck AG, Darmstadt, 2nd edn., p. 30.

¹¹ Foster, *Chem. and Ind.*, 1952, 828.

¹² Foster, *J.*, 1953, 982.