NOTES.

309. *Cyclisation and Debenzylation of* m-*Benzyloxyphenylpropionic Acid as Competitive Reactions.*

By M. DONBROW.

DURING an investigation into ring-closures yielding 5-alkyloxyindan-1-ones attempts were made to cyclise *m*-benzyloxyphenylpropionic acid by Friedel–Crafts methods. Aluminium chloride invariably caused debenzylation but significant amounts (10—15%) of 5-benzyloxyindan-1-one survived when stannic chloride dissolved in benzene was used and the main product, 5-hydroxyindan-1-one, was relatively pure and in good yield (40—50%). The 5-benzyloxyindan-1-one was identical with a sample prepared by direct benzylation of 5-hydroxyindan-1-one. The partial retention of the benzyloxy-group and the clean debenzylation were considered to warrant the use of this system to study cyclisation and debenzylation as competitive reactions.

The reactions were followed by quantitative analysis of the products, the experiments being designed to test variables such as concentration of reactants, excess of reagents, time, temperature, and solvent composition. Separation of the product into acidic, phenolic ketonic, phenolic non-ketonic, neutral ketonic, neutral non-ketonic, and ether-insoluble polymeric fractions revealed considerable complexity. The neutral fraction contained, in addition to the required ketone, traces of higher-melting ketones, diphenylmethane, and occasionally benzyl chloride. The phenolic ketone, mainly 5-hydroxyindan-1-one, contained other ketones, one of which was probably a benzyl-substituted hydroxyindan-1-one $C_{16}H_{14}O_2$. Traces of 7-hydroxyindan-1-one derivatives were also detected. A violet complex always separated during the reaction and since a similar complex was precipitated during the cyclisation of the 5-methoxy-analogue (which was not however demethylated), the violet compound was presumed to be a ketone–catalyst complex and not an ether–catalyst compound. Retention of the benzyl group was associated with the use of a large excess of stannic chloride and the rapid separation of the violet complex, though a connection between the two could not be proved. The use of less than 1·5 mol. of stannic chloride resulted in a substantial recovery of acid, even at high temperatures. The course of the reaction was influenced by changes in scale and apparatus. Both cyclisation and debenzylation were inhibited at 0°, for 30% of the product was acidic after 18 hr. (with 2·3 mol. of catalyst) and, of the remainder, the phenolic fraction constituted 15% (w/w) instead of the 35—50% obtained between 5° and 15°.

The lag between mixing of the reactants (both dissolved in benzene) and separation of the complex varied between a few seconds and some minutes but no consistent temperature–time or concentration–time pattern was discernible. Since rapid elimination of the ketone–reagent complex favours retention of structure, the solubility of the complex is of prime concern and an attempt was made to vary the solubility by using mixtures of light petroleum, benzene, and chloroform as solvents.

The use of a large proportion of chloroform reduced precipitation and greatly increased the ratio of phenolic to neutral product (2 : 1), indicating increased debenzylation. The reverse effect could not be demonstrated because, unless the chloroform or benzene predominated, side-reactions became serious and the product complex and difficult to separate. The proportion of polymer was much higher in light petroleum and chloroform at 5° than in benzene. However, in benzene diphenylmethane was formed and constituted up to 35% of the neutral fraction. The alternative formation of diarylmethanes in the presence of, and polymers in the absence of, aromatic hydrocarbons has also been noted by Praill [1] in work on benzyl derivatives.

Other cyclising agents were tried under conditions milder than those normally employed; these included phosphorus oxychloride,[2,3] phosphoric oxide,[4,5] polyphosphoric acid,[6] anhydrous hydrofluoric acid,[7] and fluorosulphuric acid.[8] All gave viscous, non-ketonic products except the last, which in dilute chloroform solution at 0° gave small yields of very pure 5-benzyloxy- and 5-hydroxy-indan-1-one. The main reaction was evidently sulphonation, since most of the product was water-soluble.

Experimental.—m-*Benzyloxyphenylpropionic acid.* *m*-Hydroxyphenylpropionic acid [9] (30 g.) and pyridine (2 drops) were dissolved in a solution of sodium ethoxide [from sodium (9 g.)] in ethanol (200 ml.). Benzyl chloride (22·5 ml.) was added to the boiling solution which, refluxed for 1 hr., evaporated, diluted with water, washed with ether, chilled, and acidified, yielded m-*benzyloxyphenylpropionic acid* (36 g., 78%) in platelets, m. p. 86° (from dilute ethanol or acetic acid), b. p. 170°/0·05 mm. (Found: C, 75·2; H, 6·3%; titration equiv., 259. $C_{16}H_{16}O_3$ requires C, 75·0; H, 6·3%, equiv., 256). A portion was debenzylated with hydrobromic acid in acetic acid, yielding *m*-hydroxyphenylpropionic acid, m. p. 111—112°, not depressed on admixture with starting material.

5-*Benzyloxyindan*-1-*one*. (*a*) 5-Hydroxyindan-1-one [7] (1 g.) was refluxed with a solution of sodium ethoxide [from sodium (0·155 g.)] in ethanol (15 ml.) until it dissolved, and treated with freshly-redistilled benzyl chloride (0·86 g.) in ethanol (10 ml.). The mixture was refluxed for 1½ hr. and evaporated. Water was added, and the product extracted with ether, yielding 5-*benzyloxyindan*-1-*one* (0·93 g., 58%) as pale yellow prisms, m. p. 105·5—106° (from methanol) (Found: C, 81·1; H, 5·7. $C_{16}H_{14}O_2$ requires C, 80·7; H, 5·9%). The semicarbazone had m. p. 231° (from ethanol).

(*b*) *Cyclisation with stannic chloride.* *m*-Benzyloxyphenylpropionic acid (2·5 g.) in ether (12 ml.) was refluxed for 3 hr. with thionyl chloride (4 ml.) containing a trace of pyridine. After evaporation twice with benzene and ether, the acid chloride was substantially pure (Found: Cl, 12·7%; equiv., 140·2. $C_{16}H_{15}O_2Cl$ requires Cl, 12·9%; equiv., 137·4). It decomposed at 195°/0·25 mm.

The acid chloride from 2·5 g. of *m*-benzyloxyphenylpropionic acid in benzene (12 ml.) was

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[1] Praill, *J.*, 1957, 3162.
[2] Freeman and Amstutz, *J. Amer. Chem. Soc.*, 1950, **72**, 1526.
[3] Albert and Linnell, *J.*, 1936, 88.
[4] Perkin and Robinson, *J.*, 1907, **91**, 1073, 1080, 1094.
[5] Birch and Smith, *J.*, 1951, 1885.
[6] Horning and Parker, *J. Amer. Chem. Soc.*, 1952, **74**, 3870.
[7] Johnson, Anderson, and Shelberg, *ibid.*, 1944, **66**, 218.
[8] Baker, Coates, and Glockling, *J.*, 1951, 1376.
[9] Donbrow and Linnell, *J. Pharm. Pharmacol.*, 1952, **4**, 118.

treated with freshly-redistilled stannic chloride (2·5 ml.) in benzene (7·5 ml.) at 2—4°. A violet sludge was deposited. After 15 min. this was decomposed with crushed ice, hydrochloric acid, and ether. The ether–benzene layer was filtered, washed with 5% sodium hydrogen carbonate solution, dilute sodium hydroxide solution, and water and evaporated, yielding a brown, mobile liquid (1·4 g.) from which 5-benzyloxyindan-1-one (0·2 g.) crystallised at 0°, a second crop (0·2 g.) being obtained after removal of diphenylmethane from the residue by distillation or crystallisation. It formed pale yellow prisms, m. p. 105·5—106° (from methanol or ethanol), not depressed on admixture with a sample obtained by benzylation (Found: C, 81·0; H, 5·9%). Its *semicarbazone* had m. p. 231° (from ethanol), not depressed on admixture with a sample from benzylation (Found: C, 69·8; H, 5·9; N, 14·1. $C_{17}H_{17}O_2N_3$ requires C, 69·2; H, 5·8; N, 14·2%).

From the aqueous alkaline extracts, 0·7 g. of an impure phenol, obtained on acidification and extraction with ether, yielded large crystals of 5-hydroxyindan-1-one,[7,10,11] m. p. 185° (from methanol). Its semicarbazone had m. p. 223°.

Cyclisations.—These were carried out on the 2·5 g. scale, conditions being varied as described in the Introduction. Some larger-scale runs (10 and 15 g.) were carried out. The acid chloride was freshly prepared in large batches, evaporated twice with solvent, and analysed before use.

The fractions were separated into acidic, phenolic, and neutral components and insoluble polymer. The uncrystallisable residues were checked for ketones and separated by use of Girard's reagent P into ketonic and non-ketonic fractions. Tests applied were (1) colour reaction with alcoholic ferric chloride (for 7-hydroxyindan-1-ones),[10] (2) reaction with hydriodic acid (for odour of benzyl iodide), (3) oxidation with chromic acid and reaction of products with Brady's reagent (for benzyl derivatives of non-ketonic fractions).[12,13] Traces of unidentified ketones were obtained together with a *benzyloxyindan-1-one* (?), pale yellow prisms, m. p. 220—224° (from ethanol), insoluble in water, soluble in sodium hydroxide solution; no colour with ferric chloride solution (Found: C, 80·3; H, 5·98%), 2 : 4-dinitrophenylhydrazone, m. p. 236—242° (decomp.) (from glacial acetic acid), 235—241° decomp. (from ethyl acetate).

I thank Prof. W. H. Linnell for his interest and advice.

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[10] Ingold and Pigott, *J.*, 1923, 1469.
[11] Brand and Horn, *J. prakt. Chem.*, 1927, **115**, 351, 376.
[12] Burton and Praill, *J.*, 1951, 522.
[13] *Idem*, *J.*, 1953, 827.

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310. *A Quantitative Ullmann Reaction.*

By P. H. GORE and (the late) G. K. HUGHES.

THE formation of diphenyls in the Ullmann reaction[1] has been much studied. Recently, Carlin and Foltz[2] have reported yields of the diphenyls of 46% from 1-iodo-4- and of 79% from 1-iodo-6-methyl-2-nitrobenzene, using 1 equiv. of copper powder, and, in the latter case, sand as a diluent to moderate the reaction. Earlier, Wittig and Stichnoth[3] obtained a similar yield (81%) in the latter reaction by careful addition of the copper, without the use of diluent. For the preparation of 2 : 2′-dinitrodiphenyl from *o*-iodonitrobenzene, Davey and Latter[4] recorded a yield of 65%. We have found that commercial samples of copper powder give irreproducible yields in this reaction, and that freshly precipitated copper, obtained by a modification of Ritchie's method,[5] is the most effective.

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[1] Fanta, *Chem. Rev.*, 1946, **38**, 139.
[2] Carlin and Foltz, *J. Amer. Chem. Soc.*, 1956, **78**, 1997.
[3] Wittig and Stichnoth, *Ber.*, 1935, **68**, 930.
[4] Davey and Latter, *J.*, 1948, 264.
[5] Ritchie, *J. Proc. Roy. Soc., N.S.W.*, 1945, **78**, 161.

By the use of approx. 4 equiv. of copper, and of careful temperature control, yields of 95—97% of 2 : 2′-dinitrodiphenyl were reproducibly obtained.

Experimental.—*Copper powder.* Oxide-free zinc dust was added to an excess of slightly acidified aqueous copper sulphate, the temperature not being allowed to rise above 40°. The precipitated copper was collected, washed free from copper and acid, and twice with dry acetone, and dried at 100°.

2 : *2′-Dinitrodiphenyl.* Copper powder (30 g.) was added in small portions, with occasional stirring, to *o*-iodonitrobenzene (30 g.) in a thick-walled conical flask kept at 190°. After 2½ hr. at 190°, heating was continued at 240° for 2½ hr. The product was extracted with hot benzene, the filtered extract on evaporation giving substantially pure 2 : 2′-dinitrodiphenyl (29·2 g., 96%; m. p. 122—124°, or 124° after one crystallisation from ethanol).

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311. 1- *and* 2-*Anthraldehydes.*

By P. H. Gore.

In connection with other work, the syntheses of 1- and 2-anthraldehydes were investigated. Attempted preparation of 1-anthraldehyde by the Stephen reduction [1] of 1-anthronitrile proved abortive; this is in keeping with the observation [2] that in this reaction 1-naphthaldehyde is formed only to about 7% under conditions which give a 91% yield of 2-naphthaldehyde.

1- and 2-Anthronitriles were converted into the corresponding aldehydes by use of a deficiency of lithium aluminium hydride, a method which was successful in the preparation [3] of benzaldehyde and 2-naphthaldehyde in good yield. Addition of benzene was necessary to increase the solubility of the anthronitriles in ether, but more than 30% (by volume) precipitated the hydride and reduction did not take place. Even then, reduction was incomplete, and large amounts of the anthronitriles were recovered. The aldehydes were isolated as 2 : 4-dinitrophenylhydrazones, which were readily separable from nitriles. Regeneration was by use of pyruvic acid.[4]

Light absorption of some anthracene derivatives [a] (λ *in* Å).

	1-Anthryl				2-Anthryl			
Derivative	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{max.}$	$\varepsilon_{max.}$
Chloro-	2500	93,800 [b]	3650	6,400	2555	153,000 [3]	3600	5,750
	2570	105,000	3840	5,750	3280	1,900	3800	4,900
	3480	4,050			3420	3,300		
Nitrile	2570	87,200	3780	6,050	2510	73,000 [c]	3580	4,100
	3580	4,500	3960	5,100	2570	103,000	3760	3,750
					2640	73,000	3920	2,600
					3430	3,000		
Aldehyde	2430	55,700	3680	3,700	2590	61,800	3430	4,300
	2640	51,600	3970	4,750	2650	61,800	3640	4,300
	2800	24,400			2700	57,800	3840	3,700
					2810	51,500	4050	2,800
					3280	2,800		
Aldehyde 2 : 4-dinitrophenylhydrazone			4300	23,200	3960	28,400		

[a] In chloroform, unless otherwise stated. [b] Inflection. [c] In ethanol

The analytical figures obtained for the 2-anthraldehyde are 1·5% low for carbon, possibly owing to contamination by 2-anthroic acid. There is little doubt as to its chemical

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[1] Stephen, *J.*, 1925, **127**, 1874; cf. Leber, *J. Amer. Chem. Soc.*, 1949, **71**, 2862.
[2] Williams, *ibid.*, 1939, **61**, 2248.
[3] Braude and Gore, *J.*, in the press.
[4] Mattox and Kendall, *J. Amer. Chem. Soc.*, 1948, **70**, 882.

identity, however, since it can be reconverted into its dinitrophenylhydrazone in high yield.

The starting materials were 1- and 2-chloroanthracene,[5] which were converted into the nitriles by cuprous cyanide in dry pyridine.[6-8] Overall yields were about 20% for the four stages from the chloroanthraquinones.

Light-absorption data are given in the Table; there were no unexpected features. The position of the *K*-band of the two dinitrophenylhydrazones [9] points to a greater conjugating power of the 1- than of the 2-anthryl position, as expected from theory.[10]

EXPERIMENTAL

The microanalyses were by Mr. F. H. Oliver and his staff and the light-absorption measurements by Mrs. I. Boston, of the Department of Chemistry, Imperial College.

1-*Chloroanthracene*.—The method of Fischer and Ziegler [5] was used. The yield was increased to 92% by heating the mixture for 3 hr. instead of 0·5 hr. The product formed yellow crystals, m. p. 81° (quoted [5] m. p. 79°).

1-*Anthronitrile*.—1-Chloroanthracene (16 g.) and cuprous cyanide (8·2 g.) were heated with pyridine (16 ml.) (freshly distilled from potassium hydroxide) at 245—255° (bath temp.) for 24 hr. During the last hour the pyridine was allowed to distil off. After cooling, the dark residue was repeatedly extracted with hot alcohol, the extracts were evaporated to dryness, and the residue chromatographed from benzene on alumina. The eluate yielded nearly pure 1-anthronitrile (13·5 g., 89%), m. p. 137—138°, which on recrystallisation afforded yellow plates, m. p. 139—140° (Found: C, 89·0; H, 4·7; N, 6·5. Calc. for $C_{15}H_9N$: C, 88·6; H, 4·5; N, 6·9%) (Dieuel [11] quotes m. p. 126°):

1-*Anthraldehyde* 2 : 4-*Dinitrophenylhydrazone*.—1-Anthronitrile (10 g.) was dissolved in ether (350 ml.)–benzene (150 ml.), and to the stirred solution at 0°, lithium aluminium hydride (1·05 g.) in ether (100 ml.) was added during 5 min. After being stirred and heated under reflux for 1 hr., the mixture was set aside for 12 hr. It was then again cooled to 0°, and excess of 2N-sulphuric acid was carefully added. The organic layer was separated, washed, and evaporated. The residual solid, in hot alcohol, was treated with a large excess of ethanolic 2 : 4-dinitrophenylhydrazine sulphate. Extraction of the red precipitate (9·5 g.) with boiling methanol (300 ml.), filtration whilst hot, and cooling gave 1-anthronitrile (5·4 g.; m. p. 138—140°) and left undissolved 1-*anthraldehyde* 2 : 4-*dinitrophenylhydrazone* (3·2 g., 37% after allowance for recovered anthronitrile), m. p. 279—281°. Crystallisation from pyridine gave bright red plates, m. p. 282—283° (Found: C, 65·1; H, 4·2; N, 14·4. $C_{21}H_{14}O_4N_4$ requires C, 65·3; H, 3·7; N, 14·5%).

1-*Anthraldehyde*.—The 2 : 4-dinitrophenylhydrazone (4·0 g.) was suspended in chloroform (75 ml.); 90% pyruvic acid (8 ml.) and acetic acid saturated with hydrogen bromide (5 ml.) were added, and the mixture was gently boiled for 17 hr. The mixture was cooled, and extracted with water, aqueous sodium hydrogen carbonate, and again with water, dried (Na_2SO_4), and evaporated. Chromatography from benzene on alumina, followed by crystallisation from acetone, and finally from carbon tetrachloride, gave large dark red prisms of 1-*anthraldehyde* (1·35 g., 64%; m. p. 126·5—127·5°) (Found: C, 87·0; H, 5·1. $C_{15}H_{10}O$ requires C, 87·4; H, 4·9%). There was no reaction with sodium hydrogen sulphite.

2-*Chloroanthracene*.—Prepared by the method of Fischer and Ziegler,[5] but with 6 hours' heating, the 2 chloro-compound was obtained in 83% yield. Purified by chromatography on alumina and recrystallisation from acetic acid the product had m. p. 217—218° (quoted [5] m. p. 215°). In benzene solution, it exhibits an intense violet fluorescence.

2-*Anthronitrile*.—This was prepared as described for the 1-isomer and obtained in 81% yield. After recrystallisation from acetic acid it had m. p. 200° (quoted [12] m. p. 200°).

2-*Anthraldehyde*.—The method used was identical with that described for the 1-isomer. The

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[5] Fischer and Ziegler, *J. prakt. Chem.*, 1912, 2, **86**, 293.
[6] Cf. Beyer and Fritsch, *Ber.*, 1941, **74**, 494.
[7] Newman, *J. Amer. Chem. Soc.*, 1937, **59**, 2472.
[8] Schultz, Goldberg, Ordas, and Carsch, *J. Org. Chem.*, 1940, **11**, 307.
[9] Braude and Jones, *J.*, 1945, 498.
[10] Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1947, *A*, **192**, 16.
[11] Dieuel, *Ber.*, 1906, **39**, 926.
[12] Waldmann and Oblath, *Ber.*, 1938, **71**, 366.

2 : 4-*dinitrophenylhydrazone* (31%, based on nitrile consumed) formed deep orange tufts (from pyridine–ethanol), m. p. 297—298° (Found: C, 65·6; H, 4·1; N, 14·9%). 2-*Anthraldehyde* (82%) had m. p. 203—204° after recrystallisation from acetone–ethanol) (Found: C, 85·8, 85·9; H, 4·9, 5·0%).

This work was begun during the tenure of a C.S.I.R.O. studentship (P. H. G.). I thank Imperial Chemical Industries Limited, Dyestuffs Division, and Dr. R. S. Barnes, for generous gifts of 1- and 2-chloroanthraquinone, and acknowledge advice from (the late) Professor E. A. Braude.

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312. *The Dielectric Constant of Ethyl Chloride.*

By W. R. Longworth and P. H. Plesch.

The dielectric constant of liquid ethyl chloride has not been reported. As we required this in connection with other work, we measured it with Bender's apparatus,[1] using a closed cell with concentric cylindrical electrodes. It was calibrated with carbon tetrachloride (17·6°), chloroform (17·2°), methylene dichloride (0° and 17·2°), and ethylene dichloride (16·9°), by using the known dielectric constants of these substances at the given temperatures.[2] The ethyl chloride was a commercial product, f. p. —136·0° ± 0·2° (lit.,[3] f. p. —136·4°), having a completely flat freezing curve. Temperatures were measured with a pentane thermometer, which was calibrated by the freezing points of water and of specially purified specimens of carbon tetrachloride (—23·0°) and methylene dichloride (—96·7°).

The results (Table) can be represented by the equation

$$\varepsilon_{t'} = \varepsilon_t - 5{\cdot}93 \times 10^{-2}(t' - t)$$

where ε_t and $\varepsilon_{t'}$ are the dielectric constants at temperatures t and t'. The interpolated value of ε at 0° being used, this can be written for convenient use in the form

$$\varepsilon_t = 12{\cdot}25 - 5{\cdot}93 \times 10^{-2}t$$

where t is in ° c. We estimate the uncertainty in the dielectric constant values to be less than ±2%.

Temp.		−72°	−65°	−47°	−34°	−32°	−22°	−12°	−2°
Dielectric constant	Run 1	—	—	15·05	14·30	—	13·55	12·95	12·50
	Run 2	—	—	15·15	—	14·30	13·55	12·95	12·50
	Run 3	16·50	16·10	15·05	—	14·30	13·55	12·80	12·35

We acknowledge grants from Esso Research Limited (to W. R. L.).

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[1] Bender, *J. Chem. Educ.*, 1946, **23**, 179.
[2] National Bureau of Standards, Circular 514.
[3] Timmermans, " Physico-Chemical Constants of Pure Organic Liquids," Elsevier Publ. Co. Inc., New York, 1950.

313. *Characterisation of Aromatic Amines by* p-p′-*Nitrophenylazobenzoyl Derivatives.*

By El S. Amin.

p-*p*′-Nitrophenylazobenzoyl chloride, already used for identification and separation of alcohols [1] and aliphatic amines,[2] has now been similarly applied to aromatic amines. The chloride has given acyl derivatives in fairly good yields on reaction with nine aromatic amines in pyridine–benzene at convenient temperatures. The acyl derivatives melt sharply and at much higher temperatures (in a convenient range) than do other derivatives.[3,4] Moreover, the m. p.s differ sufficiently to be useful criteria. *o*-Aminophenol reacted with the reagent to produce both *N*- and *O*-acyl compounds whereas *p*-phenylazobenzoyl chloride does not.[3] Occasionally contaminating nitrophenylazobenzoic acid has to be removed chromatographically. The acyl derivatives are bright red, an advantage in chromatography.

Experimental.—Evaporations were under reduced pressure at 50°. M. p.s were determined on a Kofler microscope stage.

Preparation of acyl derivatives. The aromatic amine (0·5 mmole) and *p*-*p*′-nitrophenylazobenzoyl chloride [1] (0·725 mmole) were refluxed in 1 : 1 pyridine–benzene (100 ml.) for 6 hr. The mixture was treated with water and extracted with 1 : 1 benzene–ether (250 ml.). The extract was washed with 20% sulphuric acid, filtered, washed with water, aqueous sodium carbonate, and water, concentrated to *ca.* 50 ml., and filtered through activated alumina. The main, lower red band was eluted with benzene, and the product recrystallised from acetone (as needles). The *p*-*p*′-nitrophenylazobenzoyl derivatives shown in the Table were thus prepared in 90—95% yield. The first seven were recrystallised from acetone, and the last two from dimethylformamide.

Acyl derivatives, $NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}CO{\cdot}NHR$.

			Found (%)				Required (%)		
Aromatic amine	Colour of deriv.	M. p.	C	H	N	Formula	C	H	N
Aniline	Orange	270°	65·8	4·2	16·4	$C_{19}H_{14}O_3N_4$	65·9	4·1	16·2
o-Anisidine	Orange-red	228	—	—	14·9	$C_{20}H_{16}O_4N_4$	—	—	14·9
β-Naphthylamine	Orange	270	—	—	13·9	$C_{23}H_{16}O_3N_4$	—	—	14·1
α-Naphthylamine	Orange	263	69·8	4·1	13·7	$C_{23}H_{16}O_3N_4$	69·7	4·1	14·1
o-Toluidine	Orange	224	66·9	4·5	—	$C_{20}H_{16}O_3N_4$	66·7	4·5	—
m-Toluidine	Orange	208	66·8	4·6	—	$C_{20}H_{16}O_3N_4$	66·7	4·5	—
p-Toluidine	Orange	308	66·5	4·4	—	$C_{20}H_{16}O_3N_4$	66·7	4·5	—
o-Phenylenediamine	Red	306	62·1	3·7	18·0	$C_{32}H_{22}O_6N_8$	62·5	3·6	18·2
o-Aminophenol	Red	240	62·3	3·9	—	$C_{32}H_{21}O_7N_7$	62·4	3·4	—

Hydrolysis by potassium hydroxide (1 mole) in 2-methoxyethanol for a few hours at 50° regenerated the aromatic amine.

Chromatography. The two layers formed by a 5 : 1 (v/v) mixture of 65% aqueous dimethylformamide and carbon tetrachloride were separated. A tube (*ca.* 40 cm. long, 2 cm. diam.) was half filled with the dimethylformamide layer. A 1 : 1 (w/w) mixture (20 g.) of the other layer and kiesulguhr impregnated with dimethyloxosilane [2] was made into a sludge with the carbon tetrachloride layer (40 c.c.) and added to the column. When the column had drained, the acyl derivatives (2 mg.), dissolved in the carbon tetrachloride layer, were added and the chromatogram was developed with the dimethylformamide layer under slight suction. Elution can be hastened with 75% dimethylformamide.

Nearly a complete separation was achieved of the derivatives of (i) aniline and *o*-anisidine; (ii) *o*-aminophenol and *o*-phenylenediamine; (iii) di-*n*-butylamine and α-naphthylamine; (iv) *o*-, *m*-, and *p*-toluidine.

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[1] Hecker, *Chem. Ber.*, 1955, **88**, 1666; Amin and Hecker, *ibid.*, 1956, **89**, 695.
[2] Amin, *J.*, 1957, 3764.
[3] Woolfolk and Riberts, *J. Org. Chem.*, 1956, **21**, 436.
[4] McElvain, " The Characterisation of Organic Compounds," Macmillan, New York, 1946.

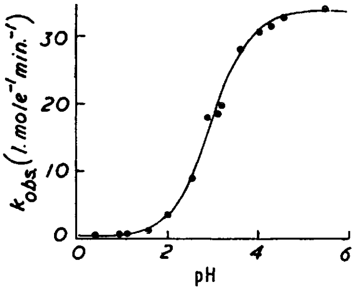
314. *Catalysis by Lead Ion of the Formation of Ethylenediaminetetra-acetatocobalt*(III) *from the Corresponding Monobromo-complexes.*

By W. C. E. HIGGINSON and M. P. HILL.

IDENTICAL first-order rate constants, $k = -\mathrm{d}\ln[(\mathrm{H})\mathrm{CoYBr}]/\mathrm{d}t$, have been found[1] for the formation in aqueous solution of the sexidentate complex ion ethylenediaminetetra-acetatocobalt(III), CoY^-, by elimination of the ligand Br^- from the corresponding quinquedentate complexes, CoYBr^{2-} and HCoYBr^-. (The value of the rate constant quoted in ref. 1 is erroneous and should read 4×10^{-4} min.$^{-1}$.) The unbound carboxylate group present in CoYBr^{2-}, and the carboxylic acid group present in the conjugate acid, HCoYBr^-, evidently take no part in the rate-determining step in these reactions.

The formation of CoY^- from these complexes is strongly catalysed by Ag^+ and Hg^{2+}.[2] Lately it has been reported[3] that Cd^{2+}, Zn^{2+}, and Fe^{3+} are effective catalysts, although less so than Ag^+ and Hg^{2+}. These observations are confirmed by our recent experiments; we also find that Tl^{3+} is very effective.

In a more detailed investigation of the kinetics of reaction between excess of Pb^{2+} and these bromo-complexes in aqueous perchlorate solutions, we find a variation in the second-order rate constant, $k_{\mathrm{obs.}} = -[\mathrm{Pb}^{2+}]^{-1}\mathrm{d}\ln[\text{bromo-complex}]_{\text{total}}/\mathrm{d}t$, with pH similar to that observed in the uncatalysed elimination of $\mathrm{H_2O}$ from the quinquedentate aquo-complexes, $\mathrm{CoYH_2O}^-$ and $\mathrm{HCoYH_2O}$.[1] Similarly, we interpret the results shown in the Figure in terms of rate constants for the reaction of CoYBr^{2-} and HCoYBr^- with Pb^{2+}, and the acid dissociation constant, K, for HCoYBr^-. At 25° and ionic strength 1·0, the second-order constants, $k_1 = -[\mathrm{Pb}^{2+}]^{-1}\mathrm{d}\ln[\mathrm{CoYBr}^{2-}]/\mathrm{d}t$ and $k_2 = -[\mathrm{Pb}^{2+}]^{-1}\mathrm{d}\ln[\mathrm{HCoYBr}^-]/\mathrm{d}t$, are $33{\cdot}8 \pm 0{\cdot}3$ and $0{\cdot}15 \pm 0{\cdot}02$ l. mole^{-1} min.$^{-1}$, respectively, and $\mathrm{p}K = 2{\cdot}96 \pm 0{\cdot}03$. The theoretical line constructed from these values is shown in the Figure. In obtaining k_2 it was necessary to make a small correction for the uncatalysed reaction, the rate constant of which is *ca.* 10^{-3} min.$^{-1}$ under these conditions.



The first-order rate constant for the elimination of $\mathrm{H_2O}$ from $\mathrm{CoYH_2O}^-$ is greater than that for the corresponding reaction of $\mathrm{HCoYH_2O}$. This has been ascribed to an intramolecular $S_{\mathrm{N}}2$-type reaction in the former complex, the unbound carboxylate group displacing the ligand $\mathrm{H_2O}$.[1] The carboxylic acid group in $\mathrm{HCoYH_2O}$ is considered to take no part in the rate-determining reaction of this complex; in this case the mechanism is of the type $S_{\mathrm{N}}1$. We believe that electrostatic repulsion between the incipiently-formed Br^- and the unbound carboxylate group present in CoYBr^{2-} is responsible for the lack of participation of this group in the rate-determining step of the uncatalysed elimination reaction. We suggest that this repulsion is overcome by the presence of Pb^{2+} in the transition complex of the catalysed reaction so that the unbound carboxylate group can participate. Hence the rate of the CoYBr^{2-}–Pb^{2+} reaction will be greater than that of the HCoYBr^-–Pb^{2+} reaction in which the carboxylic acid group will still be inactive, as in the uncatalysed elimination reactions of HCoYBr^- and $\mathrm{HCoYH_2O}$. The Br^- is probably removed as the ion-pair, PbBr^+. The ratio of the rate constants for the formation of CoY^- from a quinquedentate complex and its conjugate acid appears to depend on the charge of the group eliminated from the transition complex. In the uncatalysed reactions of (i) the bromo-complexes, (ii) the aquo-complexes, and in (iii) the Pb^{2+}-catalysed reactions of the bromo-complexes,

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[1] Shimi and Higginson, *J.*, 1958, 260.

[2] Schwarzenbach, *Helv. Chim. Acta*, 1949, **32**, 839.

[3] Dwyer and Garvan, *J. Amer. Chem. Soc.*, 1958, **80**, 4480.

the species lost are (i) Br^-, (ii) H_2O, (iii) $PbBr^+$, and the corresponding ratios are (i) 1 : 1, (ii) 7 : 1, (iii) 200 : 1.

It is proposed to extend this work to include similar studies of the catalysis by other cations, in the hope of establishing a relation between their reactivity and their affinity for halide ions, and possibly also their ionic radii. As foreshadowed above, the effect of the charge of the catalyst cation is also likely to be of interest.

Experimental.—Potassium bromo(ethylenediaminetriacetatoacetic acid)cobalt(III) dihydrate was prepared and purified as previously described.[2] Other reagents were " AnalaR " or were purified by appropriate methods. Lead perchlorate was obtained in solution by dissolving freshly precipitated lead hydroxide in dilute perchloric acid. Sodium perchlorate solution was prepared by dissolving anhydrous sodium carbonate in 60% perchloric acid. Pyridinium perchlorate solution was obtained by dissolving redistilled pyridine in dilute perchloric acid.

Solutions for kinetic experiments were made by dissolving a known weight of the solid bromo-complex in dilute perchloric acid (pH 0·4—3) or pyridine–pyridinium perchlorate buffer mixtures (pH 3—5·5). The ionic strength was made 1·0 by the addition of sodium perchlorate solution. The pH of the solution was measured by meter at the beginning and end of each kinetic experiment. The meter was standardised against a 0·01M-perchloric acid solution containing 0·99M-sodium perchlorate; the pH of this solution was taken as 2·00. Initial concentrations of the bromo-complex were 0·5—2·0 × 10^{-3}M, and of Pb^{2+}, 0·5—8·0 × 10^{-2}M. The highest concentration of free pyridine was *ca.* 0·02M, present in the solutions of highest pH, and the highest concentration of pyridinium ion was 0·2M, in a solution of pH 3·1.

The reaction was followed spectrophotometrically (Unicam S.P. 500) by measurements at 535 mμ, the molecular extinction coefficients of CoY^- and $CoYBr^{2-}$ (or $HCoYBr^-$) at this wavelength being 337 and *ca.* 90, respectively. Other measurements at 574 mμ, at which wavelength the molecular extinction coefficients are identical (230), showed that the extent of side-reactions is small. Pb^{2+} being in considerable excess, plots of $\ln (D_\infty - D_t)$ against t were linear up to *ca.* 75% of reaction, D_∞ representing the optical density of the reaction solution in a given cell at the completion of reaction and D_t the optical density in the same cell at time t. Values of $k_{obs.}$ were obtained by dividing the negative gradients of these plots by the corresponding concentrations of Pb^{2+}. Experiments with different pyridine–pyridinium ion buffer concentrations, but similar pH values, showed that the rate of reaction was little affected by the concentration of the buffer. This buffer was used instead of the commoner acetate–acetic acid buffer in order to avoid the complication of complex formation between Pb^{2+} and acetate ions, the formation constant for $(PbCH_3{\cdot}CO_2)^+$ being *ca.* 100.[4]

The apparent p*K* of $HCoYBr^-$ was found to be 2·96 ± 0·03 at 25° and ionic strength 1·0 by pH titration, the meter being standardised as described above. The pH of this complex has previously been found to be 2·98 ± 0·05 at 20° and ionic strength 0·1.[5]

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

[4] Edmonds and Birnbaum, *ibid.*, 1940, **62**, 2367.
[5] Schwarzenbach and Heller, *Helv. Chim. Acta*, 1951, **34**, 576.

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315. *Electronic Structure, Chemical Reactivity, and Basicity of Purines and Pyrazolopyrimidines.*

By BERNARD PULLMAN.

MY collaborators and I have studied recently, by the molecular-orbital method, the electronic structure of fundamental natural purines[1,2] and of purine antimetabolites active in cancer chemotherapy.[3] A special study has been made of their basicity.[4] This research has been extended to pyrazolopyrimidines.[5] We now make some complementary

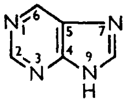
[1] Pullman, Pullman, and Berthier, *Compt. rend.*, 1956, **243**, 380.
[2] Pullman and Pullman, *Bull. Soc. chim. France*, 1958, 766.
[3] Pullman and Pullman, *Bull. Soc. chim. France*, 1958, 973.
[4] Nakajima and Pullman, *Bull. Soc. chim. France*, 1958, 1502.
[5] Pullman, Pullman, and Nakajima, *Bull. Soc. chim. France*, in the press.

remarks in connection with Lynch, Robins, and Cheng's paper on ionisation constants of purines and pyrazolopyrimidines.[6] These authors, who then only had our first note on the structure of purines,[1] state that little reliance can be placed on the results of our calculations on the purine molecule because " the calculated charge densities at the various carbon atoms predict an incorrect order of reactivities towards nucleophilic reagents." This probably refers to the observation that $C_{(6)}$-substituents in purine are attacked by nucleophils preferentially to $C_{(2)}$-substituents, although our calculations indicated that $C_{(2)}$ is the more positive. However, the *relative* charge distribution as calculated is probably reliable. The point is that this charge distribution in the *isolated molecule* should be used with care to interpret chemical reactivity, because the latter depends on the properties of the molecule *in the transition state* and, although in some cases induced polarisability runs parallel to the permanent one (as seems to be largely the case in pyrazolopyrimidines), this is not generally so.[7] This is illustrated in the Table of localisation energies[8] for nucleophilic, electrophilic, and radical attacks on $C_{(2)}$, $C_{(6)}$, and $C_{(8)}$ of purine (I), pyrazolo-(5′ : 4′-4 : 5)pyrimidine (II), and pyrazolo(4′ : 5′-4 : 5)pyrimidine (III). These energies measure approximately the relative activation energies for such attacks and, consequently, the smaller these energies the greater should be the reactivity of the corresponding carbon atoms.

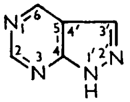
The results show that $C_{(6)}$ of purine should be more reactive towards nucleophilic attack than $C_{(2)}$ in spite of its being less positive in the isolated molecule. We have also calculated the localisation energies for nucleophilic attack on $C_{(2)}$ and $C_{(6)}$ of 2 : 6-diaminopurine as 2·730β and 2·608β respectively, again confirming the greater reactivity of $C_{(6)}$ of disubstituted purines. A striking example of a possible divergence between charge distribution and reactivity is seen in electrophilic reactions of purine: the smallest localisation energy for electrophilic attack is that of $C_{(8)}$, which should thus be the most reactive towards such an attack, although it has in the ground state of isolated purine the greatest deficiency in π-electrons. The theoretical results relating to the electrophilic localisation energy agree well with Albert's findings.[9]

		Localisation energy (in β units) for			π-Electronic charge in the isolated molecule (e)
Compound	Carbon atom	Nucleophilic attack	Electrophilic attack	Radical attack	
(I)	2	2·323	2·567	2·445	0·902
	6	2·176	2·482	2·329	0·907
	8	2·176	2·393	2·285	0·895
(II)	2	2·277	2·613	2·445	0·890
	6	2·115	2·529	2·322	0·881
	3′	2·535	2·213	2·374	1·053
(III)	2	2·359	2·609	2·484	0·910
	6	2·193	2·549	2·371	0·910
	3′	2·601	2·189	2·395	1·075

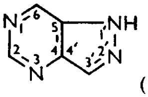
The values of the coulombic and exchange integrals adopted for the hetero-atoms are, in the usual notations, $\alpha_N = \alpha_C + 0{\cdot}4\beta_{C-C}$, $\alpha_{N-H} = \alpha_C + \beta_{C-C}$, $\beta_{C-N} = \beta_{C-C}$, $\beta_{C-NH} = 0{\cdot}9\beta_{C-C}$. The absolute values of the polarisation energies depend of course on the precise values of these parameters. Nevertheless, the relative values of these energies, which alone interest us here, are to a very large extent independent of the precise values of the parameters.



(I)



(II)



(III)

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[6] Lynch, Robins, and Cheng, *J.*, 1958, 2973.

[7] See, *e.g.*, Pullman, *Cahiers Phys.*, 1954, **48**, 42.

[8] Wheland, *J. Amer. Chem. Soc.*, 1942, **64**, 900; Pullman and Pullman, " Les Théories Electroniques de la Chimie Organique," Masson, Paris, 1952, Chap. X; " Cancérisation par les Substances Chimiques et Structure Moléculaire," Masson, Paris, 1955, Chap. II.

[9] Albert, in " The Chemistry and Biology of Purines," Ciba Foundation Symposium, Churchill, London, 1957, p. 97.

A similar situation holds for the basicity of the ring nitrogen atoms which does not depend necessarily on the electrical charge of these atoms but must be calculated in a suitable way.[10] Thus, the most basic nitrogen should be $N_{(1)}$ in purine and adenine and $N_{(7)}$ in guanine,[4] although these are not the most charged nitrogen atoms in these molecules. Under the assumption that reactivity is correlated with the stability of the Wheland-type transition state,[8] these predictions are verified by recent experimental results such as the formation of adenine N^1-oxide [11] or the preferential reactivity of $N_{(7)}$ of guanine [12] and $N_{(1)}$ of adenine [13] towards alkylating agents. In connection with Lynch, Robins, and Cheng's speculation [6] we add that our calculations [5] indicate that $N_{(1)}$ is the most basic nitrogen atom in the active antagonist 6-aminopyrazolo(5' : 4'-4 : 5)pyrimidine as well as in a number of other compounds of this group. Contrariwise, in the inactive antagonist, 6-aminopyrazolo(4' : 5'-4 : 5)pyrimidine, and in other compounds of this group, the most basic nitrogen should be, following our calculations, $N_{(3)}$. The significance of these results for the possible correlation between structure and antitumour activity of both purines and pyrazolopyrimidines is discussed in references 4 and 5.

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[10] Nakajima and Pullman, *J. Chim. phys.*, 1958, 793.
[11] Stevens and Brown, *J. Amer. Chem. Soc.*, 1958, **80**, 2759.
[12] Lawley, *Proc. Chem. Soc.*, 1957, 290; Lawley and Wallik, *Chem. and Ind.*, 1957, 633.
[13] Lawley, personal communication.

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316. *Spectral Shift in Methylpyridines.*

By ASISH KUMAR CHANDRA and SADHAN BASU.

INTRODUCTION of a methyl group into an aromatic hydrocarbon shifts the longest-wavelength absorption band. For alternant hydrocarbons the shift is bathochromic, but for non-alternant ones it may be bathochromic or hypsochromic. If it is assumed that the longest-wavelength absorption band is associated with the energy change in the transition of an electron from the highest bonding to the lowest antibonding orbital, this suggests that the methyl group changes the energy of one or both orbitals. Longuet-Higgins and Sowden [1] have worked out a simple perturbation method for calculating this change in orbital energies of aromatic hydrocarbons due to inductive and hyperconjugative effects of a methyl group or groups. It has been shown that with methylpyridines the shift is bathochromic except for 4-methylpyridine, where it is hypsochromic.[3] To find out how far Longuet-Higgins and Sowden's method enables us to estimate these shifts the present work was done. The theoretical basis of the method has been discussed in detail by Longuet-Higgins and Sowden.[1] The principles are as follows:

Inductive effect. When a ring hydrogen atom is replaced by a methyl group, the Coulomb integral of the methylated carbon atom is altered owing to the inductive effect of the electron-releasing methyl group. If a and b refer to the highest filled and the lowest empty molecular orbital respectively, the net change in transition energy due to the inductive effect is given by

$$(\Delta\varepsilon_{ab})_{\text{induc.}} = (\varepsilon_b' - \varepsilon_a') - (\varepsilon_b - \varepsilon_a) = (c_{br}^2 - c_{ar}^2)\delta\alpha_r + \left(\sum_{j\neq b}\frac{c_{br}^2c_{jr}^2}{\varepsilon_b - \varepsilon_j} - \sum_{j\neq a}\frac{c_{ar}^2c_{jr}^2}{\varepsilon_a - \varepsilon_j}\right)$$

where the primed quantities refer to methylpyridine carrying the methyl group at the rth carbon atom, and the unprimed to pyridine itself. c_{rj} refers to atomic-orbital coefficient of the rth carbon in the jth molecular orbital. $\delta\alpha_r$, the alteration in the Coulomb integral, was taken as $-0{\cdot}1\beta$. The molecular-orbital calculation on pyridine was made by the straightforward method, the Coulomb integral for nitrogen being taken as $(E_0 + 0{\cdot}66\beta)$

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[1] Longuet-Higgins and Sowden, *J.*, 1952, 1404; cf. Coulson, *Proc. Phys. Soc.*, 1952, *A*, **65**, 933.

(E_0 being the Coulomb integral for aromatic carbon), and for carbon attached to nitrogen as (E_0 +0·083β) and all resonance integrals being set equal to $\beta = \beta_{C-C}$. The effect of two or more methyl groups was considered as additive. $(\Delta\varepsilon_{ab})_{\text{induc.}}$ calculated for various mono-, di-, and tri-methylpyridines are summarised in Table 1.

Hyperconjugative effect. If pyridine and methyl group are considered as two separate conjugated systems, then it can be shown by Coulson–Longuet-Higgins perturbation treatment [2] that the orbital energies of the two systems will change if they are joined by a single bond across which conjugation can be established between the two systems. If β_{rs} is the resonance integral of the bond formed between the *r*th carbon atom of pyridine and the *s*th carbon atom of the methyl group, then Longuet-Higgins and Sowden [1] showed that the energy change due to hyperconjugative effect can be written as

$$(\Delta\varepsilon_{ab})_{\text{hypercon.}} = \beta_{rs}^{2}\left(\sum_{k \neq b} \frac{c_{br}^{2}c_{ks}^{2}}{\varepsilon_b - \varepsilon_k} - \sum_{k \neq a} \frac{c_{ar}^{2}c_{ks}^{2}}{\varepsilon_a - \varepsilon_k}\right)$$

A conjugating methyl group was considered as $-C\equiv H_3$ with the following Coulomb and resonance parameters: $E_c = E_0 - 0{\cdot}1\beta$, $\beta_{Me} = 2{\cdot}5\beta$, $E_{H_3} = E_0 - 0{\cdot}5\beta$, and $\beta_{rs} = 0{\cdot}7\beta$. As for the inductive effect, the hyperconjugative effect of more than one methyl group was also considered as additive. Calculated values of $(\Delta\varepsilon_{ab})_{\text{hypercon.}}$ are in Table 1. The mere addition of the two separate effects to get the resultant effect is justified in this approximation, so $(\Delta\varepsilon_{ab})_{\text{total}} = (\Delta\varepsilon_{ab})_{\text{induc.}} + (\Delta\varepsilon_{ab})_{\text{hypercon.}}$. Δλ is the energy difference converted into wavelength (mμ) calculated by taking β = —23,000 cm.$^{-1}$, and the found values are those of Andon, Cox, and Herington.[3]

TABLE 1. *Calculated and experimental spectral shift in methylpyridines* ($\varepsilon_b - \varepsilon_a = -1{\cdot}811\beta$).

Pyridine	$(\Delta\varepsilon_{ab})_{\text{induc.}}$	$(\Delta\varepsilon_{ab})_{\text{hypercon.}}$	$(\Delta\varepsilon_{ab})_{\text{total}}$	Δλ (calc.) (mμ)	Δλ (obs.) (mμ)
2-Methyl	+0·0123β	+0·0467β	+0·0590β	8·0	7·0
3- ,, ...	+0·0183β	+0·0409β	+0·0592β	8·1	6·5
4- ,, ...	—0·0308β	+0·0067β	—0·0241β	—3·2	—3·0
2 : 3-Dimethyl	+0·0306β	+0·0876β	+0·1182β	16·8	11·0
2 : 4- ,, ...	—0·0185β	+0·0534β	+0·0349β	4·7	3·0
3 : 4- ,, ...	—0·0125β	+0·0476β	+0·0351β	4·7	2·0
2 : 5- ,, ...	+0·0306β	+0·0876β	+0·1182β	16·8	14·0
2 : 6- ,, ...	+0·0246β	+0·0934β	+0·1181β	16·7	14·0
3 : 5- ,, ...	+0·0366β	+0·0818β	+0·1184β	16·8	12·0
2 : 3 : 6-Trimethyl ...	+0·0429β	+0·1343β	+0·1773β	26·0	19·0
2 : 4 : 6- ,, ...	—0·0062β	+0·1001β	+0·0939β	13·1	10·0
2 : 3 : 4- ,, ...	—0·0002β	+0·0943β	+0·0941β	13·2	10·5
2 : 4 : 5- ,, ...	—0·0002β	+0·0943β	+0·0941β	13·2	10·5
2 : 3 : 5- ,, ...	+0·0489β	+0·1286β	+0·1774β	26·0	20·0

Agreement between the calculated and experimental shift is fairly good. The calculation shows that the spectral shift is bathochromic for all except 4-methylpyridine, as is actually the case. Whenever the methyl group is at the 4-position the inductive effect opposes the hyperconjugative effect, but the latter outweights the former except in 4-methylpyridine.

The experimental values (Table 1) refer to methylpyridines in 0·1M-hydrochloric acid, *i.e.*, to the protonated forms. The agreement between the calculated and experimental shift is equally good for neutral forms, *i.e.*, the spectra of methylpyridines in 0·1M-sodium hydroxide. This suggests that it would be interesting to analyse the rôle of the Coulomb integral of the nitrogen atom in determining the magnitude and direction of the calculated spectral shift.* We therefore repeated the calculation for 2- and 4-methylpyridines, taking the Coulomb integral for nitrogen as E_0 +1·0β and E_0 +0·2β respectively; the results are summarised in Table 2.

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* We thank a Referee for making this suggestion.

[2] Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1947, *A*, **191**, 39.

[3] Andon, Cox, and Herington, *Trans. Faraday Soc.*, 1954, **50**, 918.

TABLE 2. *Rôle of Coulomb integral of nitrogen on the spectral shift of methylpyridines.*

Pyridine	Coulomb integral of N	$(\Delta\varepsilon_{ab})_{\text{induc.}}$	$(\Delta\varepsilon_{ab})_{\text{hypercon.}}$	$(\Delta\varepsilon_{ab})_{\text{total}}$
2-Methyl	$E_0 + 1{\cdot}00\beta$	$+0{\cdot}00999\beta$	$+0{\cdot}04854\beta$	$+0{\cdot}05858\beta$
	$E_0 + 0{\cdot}66\beta$	$+0{\cdot}01230\beta$	$+0{\cdot}04670\beta$	$+0{\cdot}05900\beta$
	$E_0 + 0{\cdot}20\beta$	$+0{\cdot}02800\beta$	$+0{\cdot}04540\beta$	$+0{\cdot}07340\beta$
4-Methyl	$E_0 + 1{\cdot}00\beta$	$-0{\cdot}03004\beta$	$+0{\cdot}00383\beta$	$-0{\cdot}02621\beta$
	$E_0 + 0{\cdot}66\beta$	$-0{\cdot}03080\beta$	$+0{\cdot}00670\beta$	$-0{\cdot}02410\beta$
	$E_0 + 0{\cdot}20\beta$	$-0{\cdot}03266\beta$	$+0{\cdot}01241\beta$	$-0{\cdot}02025\beta$

As the Coulomb integral is reduced the magnitude of the inductive and the hyperconjugative effect increases. In 4-methylpyridine the inductive effect is negative in all three cases, and its magnitude increases as the Coulomb integral is reduced, while the total effect becomes less negative. The lowering of the magnitude of total effect is understood as we expect the shift to become bathochromic when the Coulomb integral of nitrogen is set equal to E_0, *i.e.*, when we go over to benzene.* In these circumstances we also expect the inductive effect to become positive, but the reverse is the case. It is also evident from Table 2 that for 2-methylpyridine the bathochromic shift increases as the Coulomb integral on nitrogen is reduced. All these facts indicate that the calculated shift is dependent on the value of the Coulomb integral of nitrogen.

Atomic-orbital coefficients of pyridine are appended at a Referee's request. The y direction is $1 \longrightarrow 4$ in the pyridine nucleus, and values are based on E_{N} (Coulomb integral of N) $= E_0 + 0{\cdot}6600\beta$ and E_{C} (Coulomb integral of C attached to N) $= E_0 + 0{\cdot}0825\beta$.

Energy levels	Symmetry	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$
$E_0 + 2{\cdot}1837$	S_y	0·56027	0·42687	0·33667	0·30831
$E_0 + 1{\cdot}2225$	S_y	0·54867	0·15291	−0·37435	−0·61055
$E_0 + 1{\cdot}0420$	A_y	0	0·50723	0·48685	0
$E_0 - 0{\cdot}7694$	S_y	0·54540	−0·39161	−0·21180	0·55460
$E_0 - 0{\cdot}9598$	A_y	0	0·49511	−0·51570	0
$E_0 - 1{\cdot}8941$	S_y	0·29570	−0·37760	0·45061	−0·47590

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317. *Force Constants and Centrifugal Distortion in* OCS, ClCN, *and* BrCN.

By W. J. JONES, W. J. ORVILLE-THOMAS, and U. OPIK.

THE potential function is the most important single functional representation of the ground state of a molecule. The calculation of force constants is of great value in the study of molecular structure and especially of hybrid linkages, but it has been difficult to obtain precise values where sufficient isotopic frequencies are unavailable.

An unsymmetrical linear triatomic molecule of bond-lengths r_1 and r_2 and atomic masses m_1, m_2, and m_3, has two parallel stretching vibrations and the potential function governing them contains three force constants—two bond-stretching force constants, f_{11} and f_{22}, and a bond–bond interaction constant, f_{12}. Hence an infinite number of possible sets of the three force constants will reproduce the two experimental vibrational frequencies. A general method of obtaining these allowed solutions for the force constants in terms of a parameter p has been described;[1] the variation of the force constants with p for OCS is shown in the Figure. This method was applied in several cases [1,2] and a reasonable set of

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* Presented at the European Spectroscopic Conference, Freiburg i. Br., Germany, July, 1957.

[1] Orville-Thomas, *J. Chem. Phys.*, 1951, **19**, 1162.

[2] Orville-Thomas, *J.*, 1952, 2383; *Trans. Faraday Soc.*, 1953, **49**, 855.

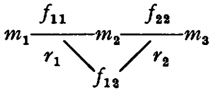
force constants chosen for each molecule by use of Gordy's relations connecting bond-order, bond-length, and force constant.[3]

Recently a new approach has become possible. Molecules are not strictly rigid and as one rotates the valence bonds and angles are distorted by centrifugal force. The extent of the distortion depends inversely upon the force constants, so knowledge of centrifugal distortion constants should yield information concerning the force field governing the vibrations of molecules.

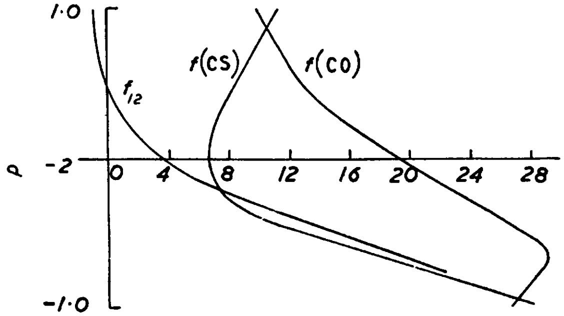
Mathematical Formulation.—When centrifugal distortion is taken into account, the frequencies of the lines in the rotational spectrum for a linear molecule are given by

$$\nu = 2B(J + 1) - 4D(J + 1)^3 \qquad [J \longrightarrow J + 1]$$

where B is related to the moment of inertia of the molecule and J is the rotational quantum number for the lower state. The centrifugal distortion constant, D, is very much smaller than the rotational constant B and accurate measurements of it have only been possible by microwave techniques.



Variation of the force constants with p in OCS.



Since centrifugal distortion only adds a small correction term to the rotational energy, a small error in the measuring of the frequencies of the microwave rotational absorption bands leads to a large error in the determination of D. As a molecule rotates faster the bonds tend to be distorted to a greater extent than for low J transitions. This increases the importance of the distortion correction term, which depends upon $(J + 1)^3$, and so accurate values for centrifugal distortion constants can be obtained by the study of higher J transitions. Many accurate values for centrifugal distortion constants have come from measurements at millimetre and submillimetre wavelengths at Duke University.

For diatomic molecules D and f are related by $D = 16\pi^2B^3\mu/f$, where μ is the reduced mass of the molecule. This expression gives force constants directly from centrifugal distortion constants from rotational spectra.

For linear triatomic molecules the position is more complicated since D depends upon three force constants as well as the moment of inertia.

Using first-order perturbation theory, Kivelson and Bright Wilson[4] obtained a general expression for the energy of a non-rigid asymmetric rotor. In their theory the effect of centrifugal distortion on the energy levels is treated as an addition perturbation in which the distortion constants enter linearly. They introduce general distortion constants $\tau_{\alpha\beta\gamma\delta}$ which are related to the moments of inertia of the molecule and the force constants occurring in the most general quadratic potential function by the equation:

$$\tau_{\alpha\beta\gamma\delta} = -\tfrac{1}{2}\sum_{i,j}\frac{1}{I_{\alpha\alpha}I_{\beta\beta}I_{\gamma\gamma}I_{\delta\delta}}\left[\frac{\partial I_{\alpha\beta}}{\partial r_i}\right]\left[\frac{\partial I_{\gamma\delta}}{\partial r_j}\right][f^{-1}]_{ij}$$

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[3] Gordy, *J. Chem. Phys.*, 1947, **15**, 305.

[4] Kivelson and Bright Wilson, jun., *J. Chem. Phys.*, 1953, **21**, 1236; 1954, **22**, 904.

where terms are as defined in ref. 4. For an unsymmetrical triatomic molecule $D = -\tau h^4/64\pi^4$ and since the system has only one moment of inertia, I, we have:

$$D = \frac{h^4}{128\pi^4 I^4}\left[\left(\frac{\partial I}{\partial r_1}\right)^2 (f^{-1})_{11} + \left(\frac{\partial I}{\partial r_2}\right)^2 (f^{-1})_{22} + 2\left(\frac{\partial I}{\partial r_1}\right)\left(\frac{\partial I}{\partial r_2}\right)(f^{-1})_{12}\right] \quad . \quad . \quad (1)$$

where $$\frac{\partial I}{\partial r_1} = 2m_1\left[\frac{(m_2 + m_3)r_1 + m_3 r_2}{m_1 + m_2 + m_3}\right]; \quad \frac{\partial I}{\partial r_2} = 2m_3\left[\frac{(m_1 + m_2)r_2 + m_1 r_1}{m_1 + m_2 + m_3}\right]$$

$$(f^{-1})_{11} = \frac{f_{22}}{f_{11}f_{22} - f_{12}^2}; \quad (f^{-1})_{22} = \frac{f_{11}}{f_{11}f_{22} - f_{12}^2}; \quad (f^{-1})_{12} = \frac{-f_{12}}{f_{11}f_{22} - f_{12}^2}$$

By substitution of the various possible sets of force constants in eqn. (1) values for D can be calculated and compared with the experimental value. Thus for a particular molecule it is possible to choose a set of force constants compatible with the infrared vibrational spectrum and which also yields distortion frequency shifts in accord with those obtained from direct analysis of the rotational spectrum.

Since the calculated value of the centrifugal distortion constant is critically dependent upon the values taken for the force constants, an accurate determination of the " best " set of force constants depends upon accurate determination of the former. Where this exists the overall accuracy in the determination of force constants is superior to that hitherto attained by the use of isotopic frequencies alone.

However, no account has been taken of the anharmonicity of the potential function. Another factor tending to limit the accuracy of the force-constant determination is the use of non-equilibrium bond lengths in the calculation.

Experimental.—Frequencies assigned to the stretching modes of some linear triatomic molecules are given in Table 1, together with bond-lengths obtained by microwave methods. From the frequencies in Table 1 various possible sets of force constants were obtained and the value of D corresponding to each set was calculated through eqn. (1). The calculated value for D is quite sensitive to the values chosen for the force constants. By comparison of the calculated D values with experimental ones the best set of force constants was chosen for each molecule (Table 2).

TABLE 1. *Bond-stretching frequencies* (*cm.*$^{-1}$) *and bond lengths* (Å) *of linear triatomic molecules.*

	ν	ν	r_1	r_2	Ref.
ClCN	2201	729	1·630	1·163	*a, b*
BrCN	2187	580	1·789	1·160	*a, b*
OCS	2064	859	1·161	1·560	*b, c*

[a] Herzberg, " Molecular Spectra and Molecular Structure," Van Nostrand, New York, 1945, Vol. 2, p. 174. [b] Smith, Ring, Smith, and Gordy, *Phys. Rev.*, 1948, **74**, 123, 370; Townes, Merrit, and Wright, *ibid.*, p. 1113. [c] Callomon, McKean, and Thompson, *Proc. Roy. Soc.*, 1951, *A*, **208**, 341.

TABLE 2. *Force constants for* ClCN, BrCN, *and* OCS.

f (10^5 dynes/cm.)				D (10^{-3} Mc./sec.)	
f_{11}	f_{22}	f_{12}		Calc.	Exptal.[a]
4·76 ± 0·02	18·45 ± 0·10	1·33 ± 0·01	^{35}ClCN, ^{37}ClCN	1·662, 1·600	$1{\cdot}66_3$, $1{\cdot}60_8$
4·00 ± 0·02	17·76 ± 0·10	0·70 ± 0·01	^{79}BrCN, ^{81}BrCN	0·8844, 0·875	$0{\cdot}884_4$, $0{\cdot}871_6$
15·35 ± 0·10	7·32 ± 0·04	0·96 ± 0·01	OC^{32}S	1·310	$1{\cdot}31_0$

[a] Burrus and Gordy, *Phys. Rev.*, 1956, **101**, 599.

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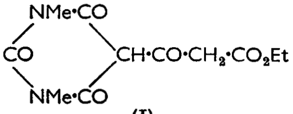
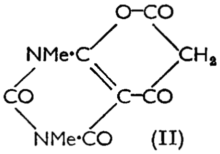
318. *Preparation of* 1 : 3-*Dimethylbarbituric Acid and Formation of* 5-*Ethoxycarbonylacetyl*-1 : 3-*dimethylbarbituric Acid.*

By J. W. CLARK-LEWIS and M. J. THOMPSON.

BARBITURIC ACIDS are usually prepared from mono- or di-substituted malonic esters and urea or substituted ureas by condensation with the aid of a sodium alkoxide, but this procedure appears less satisfactory for those acids not carrying 5-substituents, which are obtained in better yield from malonic acid and ureas with acetic anhydride as condensing agent.[1] 1 : 3-Dimethylbarbituric acid was required in larger quantities than had previously been prepared, and repetition of the synthesis according to Biltz and Wittek[1] but with sixfold quantities gave material heavily contaminated with a by-product, m. p. 112°; formation of the latter was suppressed, and a satisfactory yield of 1 : 3-dimethylbarbituric acid obtained, by adding the acetic anhydride more slowly. The structure (I) proposed for the by-product rests on elementary analysis and the titration equivalent with sodium hydroxide, which gave the empirical formula $C_{11}H_{14}O_6N_2$, and the development with ferric chloride of a red colour, indicative of the β-keto-ester structure. The main features of this structure are confirmed by formation of the compound from 1 : 3-dimethylbarbituric acid, malonic acid, and acetic anhydride; this condensation we suppose to give initially the enol lactone ester (II) which, during crystallisation from ethanol, is converted into the ethyl ester (I). The ethoxycarbonylacetyl compound (I) was hydrolysed slowly by hot concentrated hydrochloric acid to 1 : 3-dimethylbarbituric acid.



(I)



(II)

Experimental.—1 : 3-*Dimethylbarbituric acid.* Acetic anhydride (120 c.c.) was added dropwise during 3 hr. to a stirred solution of *sym.*-dimethylurea (32 g.) and malonic acid (36 g.) in acetic acid (80 c.c.). During the addition, and thereafter for 30 min., the temperature was kept at 65—70°, and the temperature was then raised and kept at 90° for 4 hr. The solution was evaporated under reduced pressure, and the residue was boiled for 15 min. with ethanol (200 c.c.); 1 : 3-dimethylbarbituric acid (33·5 g., 60%) crystallised from the cold ethanolic solution in long flat needles, m. p. 121—122° raised by recrystallisation from ethanol or benzene to 122—123° (lit.,[1] 123° and [2] 122—123°). Refrigeration of the mother liquors gave a crystalline mixture (8 g.) which yielded more (4·6 g.) dimethylbarbituric acid (total 38·1 g., 68%) after recrystallisation from benzene. Concentration of the filtrate, addition of hexane, and crystallisation of the resulting solid from ethanol gave 5-*ethoxycarbonylacetyl*-1 : 3-*dimethylbarbituric acid* in needles (2·55 g.), m. p. 110—111°, raised by recrystallisation to m. p. 112° (Found: C, 48·9; H, 5·3; N, 10·0; OEt, 14·4%; equiv., 270. $C_{11}H_{14}O_6N_2$ requires C, 48·9; H, 5·2; N, 10·4; OEt, 16·7%; equiv., 270·2). A larger yield of the by-product was obtained when the acetic anhydride was added more quickly (30 min.).

5-*Ethoxycarbonylacetyl*-1 : 3-*dimethylbarbituric acid* (I). 1 : 3-Dimethylbarbituric acid (7·8 g.), malonic acid (7 g.), acetic acid (20 c.c.), and acetic anhydride (7 c.c.) were heated at 70° for 13 hr., before evaporation under reduced pressure. The residue was boiled with ethanol (50 c.c.) for 1 hr., and 1 : 3-dimethylbarbituric acid (2·6 g.), m. p. 121—122°, crystallised from the cold solution. Refrigeration caused crystallisation of more material (3·9 g.), m. p. 70—85°, which was separated by crystallisation from benzene into 1 : 3-dimethylbarbituric acid (1·2 g.; total recovery 3·8 g., 49%), m. p. 120—122°, and 5-ethoxycarbonylacetyl-1 : 3-dimethylbarbituric acid (2·1 g.), m. p. 110—111°, after crystallisation from ethanol. The ethoxycarbonyl compound was identical with the by-product, m. p. 112°, obtained in the preparation

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[1] Biltz and Wittek, *Ber.*, 1921, **54**, 1035.

[2] Cope, Heyl, Peck, Eide, and Arroyo, *J. Amer. Chem. Soc.*, 1941, **63**, 356.

of dimethylbarbituric acid, and was very soluble in benzene, sparingly soluble in cold ethanol, and insoluble in light petroleum; an alcoholic solution of the β-keto-ester gave a red colour with ferric chloride.

Hydrolysis of 5-*ethoxycarbonylacetyl*-1 : 3-*dimethylbarbituric acid.* The ester (1 g.) was heated on a steam-bath with concentrated hydrochloric acid (20 c.c.) for 14 hr. before evaporation of the solution to dryness under reduced pressure. Crystallisation of the residue from ethanol gave 1 : 3-dimethylbarbituric acid (0·35 g., 60%), m. p. 120—122° raised by recrystallisation to m. p. and mixed m. p. 122—123°.

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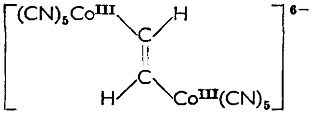
319. *An Acetylene-cyanide Complex of Cobalt*(III).

By W. P. GRIFFITH and G. WILKINSON.

DURING recent studies[1] on the pentacyanocobaltate(II) ion, it has been found that its aqueous solutions absorb various gases; we, and Winfield,[2] have observed the uptake of acetylene to give yellow solutions. From these solutions we have isolated a yellow crystalline potassium salt of stoicheiometry $K_6[Co_2(CN)_{10}C_2H_2],4H_2O$. This is diamagnetic, readily soluble in water, and thermally somewhat unstable, decomposing *in vacuo* at ~70°; it is also slowly decomposed by air. The salt was also prepared in deuterium oxide solution as $K_6[Co_2(CN)_{10}C_2H_2],4D_2O$.

It appears unlikely that in this complex ion the acetylene portion is bound to the metal atoms by donation of π-electrons from the multiple bonds to the metal atoms as in the cobalt carbonyl–acetylene complexes[3] such as $Co_2(CO)_6C_2H_2$, since such a formulation, as well as requiring a metal–metal bond, would lead to the inert-gas structure for the metal atom being exceeded.



(I; *trans*-form)

We suggest that a more reasonable structure for the complex ion is of the type (I), where a tervalent cobalt atom in an octahedral or somewhat distorted octahedral situation is bound to five cyanide groups and to an ethylene group. Such a formulation would give a diamagnetic ion with each cobalt atom having an inert-gas configuration. It may be noted that structure (I) resembles the structure recently suggested[4] for the black nitrosopentamminocobalt cation where a hyponitrito-group bridges the two cobalt atoms.

Spectroscopic studies generally support the formulation (I). Thus the high-resolution nuclear magnetic resonance spectrum (in D_2O solution) of the ion shows a single proton resonance line in the olefinic region, at 64 cycles/sec. (at 40 Mc./sec.) on the low-field side relative to water at 21° ± 1° C.

The infrared spectra of both the hydrate and the deuterate were measured. In addition to the expected absorption bands for H_2O and D_2O, there are in both compounds sharp absorption bands at 2980m, 2140vs, 2115vs, 1615m, 1120m, and 975m cm.$^{-1}$. The band at 2980 cm.$^{-1}$ is clearly assignable as a C–H stretching frequency; this value is consideraby lower than those for acetylenes, and indeed is somewhat lower than the usual frequency range for olefinic C–H stretching modes.[5] The two very strong bands at 2140 and 2115 cm.$^{-1}$ are unquestionably stretching bands for the cyanide groups. The band at 1615 cm.$^{-1}$ may be reasonably ascribed to a C=C vibration[5] and the value again indicates

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[1] Winfield, *J. Amer. Chem. Soc.*, 1958, **80**, 2060; Griffith and Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 295; Griffith, Pratt, and Wilkinson, *Nature*, 1958, **182**, 466.

[2] Winfield, personal communication.

[3] Greenfield, Sternberg, Friedel, Wotiz, Markby, and Wender, *J. Amer. Chem. Soc.*, 1956, **78**, 120.

[4] Griffith, Lewis, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 38.

[5] Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd edn., Methuen and Co., London, 1958, p. 43.

that the triple-bond character of the acetylene has been reduced in the ion to that of a double bond; the shift to lower wave numbers is greater in our ion than in the stable acetyleneplatinum complexes [6] where, however, there was only one acetylene residue per metal atom in a mononuclear complex so that the situations are of course not comparable. Although such C=C vibrations are reported to be symmetry-forbidden in the infrared region for *trans*-alkenes,[7] they do appear at low intensities in some *trans*-compounds.[8] The appearance of a fairly strong band for our ion might on this basis only imply a non-*trans*-form. The band at 1120 cm.$^{-1}$ may be attributed to an in-plane C–H deformation; although this should again be inactive in the infrared region, strong absorptions have been observed in alkenes in the 1200—1400 cm.$^{-1}$ region.[9] Finally, the band at 975 cm.$^{-1}$ may be assigned to a C–H bending mode with the hydrogen atom out of the plane of the double bond; these vibrations are known [10] to fall in the range 990—965 cm.$^{-1}$ and also to occur only for non-*cis*-types of system.[11]

Thus while we cannot be specific concerning the question of *cis*- or *trans*-structures on the basis of infrared spectra, particularly since the spectra had to be obtained in solid-state mulls, and since no other established complex of a similar type with transition metals and of known structure is available for comparison, we believe that the *trans*-form is more likely. The appearance of both the 975 cm.$^{-1}$ and the 1615 cm.$^{-1}$ band suggests that there is probably some distortion from a strictly *trans*-configuration and deviations from non-planarity about the double bond are likely. A *cis*-form, even if distorted, seems sterically unlikely in view of the presence of the approximately octahedrally disposed cyanide groups around the metal atoms.

Experimental.—Acetylene gas was passed into an air-free solution of hydrated cobaltous chloride (2·38 g., 0·01M) and potassium cyanide (3·25 g., 0·05M) with external ice-cooling. The deuterate was made similarly from anhydrous cobaltous chloride under anhydrous conditions. After a few minutes, the solution changed from deep green to straw yellow. The addition of air-free ethanol precipitated a yellow-brown oil which quickly crystallised; the crystals of *hexapotassium decacyanoacetylenedicobaltate tetrahydrate* were dissolved in water, re-precipitated from ethanol, washed with ethanol and ether, and dried under vacuum at room temperature (yield 3 g.; 85%) [Found: K, 33·8; Co, 16·6; C, 19·8; N, 20·0; H, 1·9. $K_6[Co_2(CN)_{10}C_2H_2],4H_2O$ requires K, 33·0; Co, 16·6; C, 20·3; N, 19·7; H, 1·7%].

A nickel complex was also obtained by passing acetylene into an aqueous solution of $K_4[Ni^I_2(CN)_6]$; the product was too unstable for satisfactory analysis. Its infrared spectrum and diamagnetism suggest a formulation $K_4[Ni^{II}_2(CN)_6C_2H_2]$ similar to that of the cobalt anion but with square planar (*dsp*^{2}) bivalent nickel.

Infrared measurements were made in Nujol and hexachlorobutadiene mulls on a Perkin-Elmer Model 21 instrument with NaCl and CaF_2 optics. High-resolution nuclear magnetic resonance measurements were made with the assistance of Dr. L. Pratt on a Varian Associates Model 4300 spectrometer; the samples were contained in spinning 5 mm. o.d. Pyrex sealed tubes, and the water line was used as reference.

Magnetic susceptibilities were measured on the solids by the Gouy method.

Thanks are offered to the Department of Scientific and Industrial Research for a maintenance grant (to W. P. G.).

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[*Received, December 8th*, 1958.]

[6] Chatt, Rowe, and Williams, *Proc. Chem. Soc.*, 1957, 208.

[7] Sheppard, *J. Inst. Petroleum*, 1951, **37**, 95.

[8] Jones and Sandorfy, " Chemical Applications of Spectroscopy," Interscience Publishers Inc., New York, 1956, p. 370.

[9] Sheppard and Sutherland, *Proc. Roy. Soc.*, 1949, *A*, **196**, 195.

[10] Kilpatrick and Pitzer, *J. Res. Nat. Bur. Stand.*, 1947, **38**, 191.

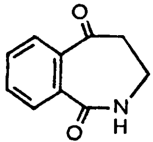
[11] Rasmussen and Brattain, *J. Chem. Phys.*, 1947, **15**, 131, 135.

320. o-*Acetylbenzamide.*

By A. H. Rees.

Karslake and Huston[1] gave no details for their original preparation of *o*-acetylbenzamide from the acid by use of phosphorus pentachloride and ammonia. Winkler[2] was unable to obtain the acid chloride, using thionyl chloride, and though Halford and Weissmann[3] seem to have prepared it successfully it gave poor yields of amides.

Since the amide was a potential intermediate for the synthesis of 2 : 3 : 4 : 7-tetrahydrobenz[*e*]azepine-4 : 7-dione (I) its preparation was re-examined, and a good yield was obtained. Its reaction with formaldehyde or formic acid in attempts at forming the azaheptacycle gave only polymers. Ring formation in two stages was therefore considered and a Mannich base was prepared from *o*-acetylbenzamide. Elimination of the secondary amine was achieved but cyclisation to (I) did not occur, resins being obtained.


(I)

o-Acetylbenzamide is not stable; it slowly polymerises.

Pilot Mannich-type reactions with *m*-hydroxyacetophenone and its benzoyl ester, aimed at the preparation of azaheptacyclic ketones, were unsuccessful, but a number of new benz[*f*]azepine derivatives has been otherwise prepared and will be reported later.

Experimental.—*o*-Acetylbenzoic acid was prepared by hydrolysis of phthaloylacetic acid obtained according to Gabriel and Neumann.[4] The latter acid is best purified by refluxing it with acetic acid in which it is sparingly soluble; a sample recrystallised from dioxan had not the quoted[5] m. p. of 243—246° but 276° as given by Röser[6] (Found: C, 62·9; H, 3·30. Calc. for $C_{10}H_6O_4$: C, 63·2; H, 3·18%).

o-*Acetylbenzamide.* The acid (32·8 g.) and thionyl chloride (55 ml.) were mixed at 30° then warmed to 40°, dissolution then becoming complete. After rapid evaporation below 30° the residue, dissolved in a little dioxan, was added to aqueous ammonia (100 ml., *d* 0·88) precooled to 5°. The mixture was rapidly evaporated, and the crude amide triturated with water then filtered off and dried *in vacuo*; yield, 20·7 g. (63%), m. p. 112°. The *semicarbazone,* m. p. 216°, crystallised from alcohol (Found: N, 25·2. $C_{10}H_{12}O_2N_4$ requires N, 25·5%).

o-*Acetyl*-N-*diethylaminomethylbenzamide.* To the above amide (16·4 g.) in alcohol were added diethylamine (7·3 g.) and formaldehyde (7·5 ml., 40%). After 2 days the solution was evaporated, leaving an oil (23·7 g.) which solidified on standing. The Mannich *base* had m. p. 118° from *iso*propyl ether (Found: C, 67·2; H, 8·09; N, 11·4. $C_{14}H_{20}O_2N_2$ requires C, 67·6; H, 8·1; N, 11·3%). The *base methiodide* had m. p. 153° from alcohol (Found: C, 46·5; H, 5·9; N, 7·2; I^-, 32·4. $C_{15}H_{23}O_2N_2I$ requires C, 46·15; H, 5·94; N, 7·2; I^-, 32·5%). The *base picrate* had m. p. 126° from alcohol (Found: N, 14·8. $C_{20}H_{23}O_8N_5$ requires N, 15·2%).

Elimination of diethylamine from the Mannich base. (a) The base (0·5 g.) was heated gently and secondary amine was evolved; the cold residue was intractable. (b) The base (2·3 g.) was refluxed in toluene to which a speck of sodium had been added, and a stream of nitrogen passed through the solution to remove the secondary amine evolved; a tar was deposited. (c) The base (3·8 g.) was shaken with dilute sulphuric acid and chloroform; evaporation of the latter after washing until neutral left a resin (2·7 g.).

m-Hydroxyacetophenone was benzoylated, and the *ester* had m. p. 52° from ether, b. p. 170°/0·3 mm. (Found: C, 75·3; H, 4·9. $C_{15}H_{12}O_3$ requires C, 75·0; H, 5·06%). Its *dinitrophenylhydrazone* had m. p. 206° from acetic acid (Found: C, 60·0; H, 3·8; N, 13·1. $C_{21}H_{16}O_6N_4$ requires C, 60·0; H, 3·8; N, 13·3%); its *semicarbazone* had m. p. 222° from dioxan (Found: N, 14·2. $C_{16}H_{15}O_3N_3$ requires N, 14·2%).

The author thanks Professors F. Bergel and C. W. L. Bevan for their interest.

University College, Ibadan, Nigeria. [*Received, December 15th,* 1958.]

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[1] Karslake and Huston, *J. Amer. Chem. Soc.*, 1909, **31**, 481.

[2] Winkler, *Ber.*, 1948, **81**, 256.

[3] Halford and Weissmann, *J. Org. Chem.*, 1952, **17**, 1646.

[4] Gabriel and Neumann, *Ber.*, 1893, **26**, 952.

[5] Michael and Gabriel, *Ber.*, 1877, **10**, 392.

[6] Röser, *Ber.*, 1884, **17**, 2620.

321. *The Preparation of Potassium Pentacyanonitrosylvanadate*(−I).

By W. P. Griffith, J. Lewis, and G. Wilkinson.

Very few nitric oxide complexes of vanadium have been characterised.[1] We have now prepared the compound $K_5[V^{-I}(CN)_5NO],H_2O$, which is a member of the isoelectronic series $[V^{-I}(CN)_5NO]^{5-}$, $[Mn^{I}(CN)_5NO]^{3-}$, $[Fe^{II}(CN)_5NO]^{2-}$; although the chromium compound $K_3[Cr^{I}(CN)_5NO],H_2O$ has been obtained,[2] we have been unable to isolate the corresponding chromium(0) compound which would be a member of this series.

The vanadium complex was prepared by the reaction of hydroxylamine hydrochloride with potassium vanadate in the presence of excess of cyanide and hydroxyl ions. It is diamagnetic and shows a N–O stretching frequency of 1575 cm.$^{-1}$, which is the lowest recorded for nitric oxide in an octahedral complex where the nitric oxide must be regarded as bonding as NO^+;[3] other strong bands in the spectrum are listed in the Table. The reason for this unusually low N–O frequency can be sought in the factors which may be considered to influence the extent of π-bonding between the metal atom and the ligands. These factors are the stereochemistry of the complex, the nature of the ligands, and the electronegativity of the metal atom. We have considered the effect of stereochemistry in nitric oxide–transition metal complexes previously.[3] The effect of the ligands for a given metal in a given oxidation state is normally quite small and is of the order of ~100 cm.$^{-1}$ as may be seen from the small variation in the N–O stretching frequencies in ruthenium complexes or in the substituted nitrosylcobalt carbonyls;[3] the frequencies in the latter compounds are given in the Table to illustrate this point.

In the series of pentacyanonitrosyl complex anions, the stereochemistry and ligand effects are constant but there is a large variation in the electronegativity of the metal atom, the formal charges on the latter varying from −1 in vanadium to +2 in iron. From the Table, it is notable that the C–N frequency does not show any substantial change whereas a large variation in the N–O frequency is observed. The small change in the C–N frequency suggests only a small change in the extent of π-bonding in the M–C–N systems. However, on decreasing the electronegativity of the metal Fe→V, the large decrease in the N–O frequency can be correlated with a greater tendency towards metal-to-nitrogen π-bonding owing to the greater availability of electron density. This would indicate that cyanide is a much better π-bonding ligand than the nitric oxide group, and it is noteworthy that the highest N–O stretching frequency occurs for a given metal in a given oxidation state in the cyanide complex, as in those of ruthenium.

There are insufficient data available on metal–ligand stretching frequencies to allow us to be certain about the above explanation. An alternative view is that the major change takes place in the extent of the metal-to-nitrogen σ-bonding on proceeding from the iron to the vanadium complex. The lower N–O stretching frequency in the latter would then arise from delocalisation of the electron density on to the oxygen atom of the nitric oxide group.

Infrared spectra of nitrosyl cyanide and carbonyl metal complexes.

Compound	Frequency (cm.$^{-1}$) N–O	C–N	Compound	Frequency (cm.$^{-1}$) N–O
$K_5[V(CN)_5NO]$	1575	2095	$NOCo(CO)_2[PPh_3]$	1754 [b]
$K_3[Mn(CN)_5NO]$	1730 [b]	2120	$NOCo(CO)[PPh_3]_2$	1754 [b]
$Na_2[Fe(CN)_5NO]$	1925 [a]	2152 [a]	$NOCo(CO)_2[Sb(C_7H_7)_3]$	1764 [b]
$NOCo(CO)_3$	1832 [b]		$NOCo(CO)_2[As(C_7H_7)_3]$	1754 [b]

[a] Herington and Kynaston, *J.*, 1955, 3555. [b] Lewis, Irving, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 32.

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[1] Addison and Lewis, *Quart. Rev.*, 1955, **9**, 115.
[2] Griffith, Lewis, and Wilkinson, *J.*, 1959, 872.
[3] Lewis, Irving, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 32.

Experimental.—Microanalyses are by the Microanalytical Laboratory, Imperial College.

Potassium pentacyanonitrosylvanadate(—I), $K_5[V(CN)_5NO],H_2O$. Ammonium vanadate (5 g.) was dissolved in a cooled solution of potassium hydroxide (15 g. in 50 ml. of water), and treated with excess of potassium cyanide solution (15 g. in 100 ml. of water). The solution was then filtered and hydroxylamine hydrochloride (8 g.) was added, whereupon the solution became deep red. It was heated on the steam-bath with occasional stirring, until no more ammonia was evolved (for about 2 hr., sufficient extra water being added at intervals to prevent any crystallisation). The cooled and filtered solution was slowly added to alcohol, and the resulting orange oil separated, washed with alcohol, dissolved in water (7 ml.), and again precipitated with alcohol. The oil was then triturated with warm absolute alcohol and ether, whereupon it quickly crystallised. This procedure was repeated, and the bright orange crystals (which are deliquescent) were dried under reduced pressure; yield, 4 g. (30%) [Found: V, 12·29; K, 46·73. $K_5[V(CN)_5NO],H_2O$ requires V, 12·01; K, 46·14%].

Physical measurements. The magnetic susceptibility was measured on the solid compound by the Gouy method. Infrared spectra were taken in Nujol and hexachlorobutadiene mulls, a Perkin-Elmer Model 21 spectrophotometer being used.

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322. *A Convenient Preparation of* o-*Aminoaryl Cyanides.*

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THE formation of *o*-aminophenyl cyanide by thermal decomposition of isatin 3-oxime [1,2] and the small-scale (0·1 g.) production of 2-amino-3-cyanonaphthalene in good yield from 5 : 6-benzisatin 3-oxime [3] have previously been reported. We now find that this reaction can be employed on a useful preparative scale both for *o*-aminophenyl cyanide and for those derivatives for which the corresponding isatins are readily accessible. Moreover, the method is applicable to the production of substituted *o*-aminoaryl cyanides having orientations not readily accessible by methods hitherto used.

Decomposition of the oximes is vigorous, and for a 50-g. quantity is complete in about 3 min. When no solvent is employed, provision must be made to trap the aminoaryl cyanide entrained in the evolved carbon dioxide. Borsche, Weussmann, and Fritzsche [1] record their failure to obtain any 2-amino-5-nitrophenyl cyanide from 5-nitroisatin 3-oxime, whereas we obtained this cyanide in satisfactory yield.

Experimental.—The substituted isatins [4] readily afforded their oximes (80—85%) on being boiled with hydroxylamine hydrochloride (1·1 mol.) in aqueous solution for 20 min.[5] It was found advantageous to recrystallise isatin 3-oxime from 50% aqueous ethanol.

2-*Aminophenyl cyanide.* Powdered isatin 3-oxime (50 g.) was placed in a 1-l. flask connected *via* a splash-head to a 2-l. two-necked flask bearing a reflux condenser connected to a Drechsel bottle containing ether. The reaction was started by melting the oxime near its upper surface and was allowed to proceed spontaneously. *o*-Aminophenyl cyanide in the Drechsel bottle, condensing system, and reaction vessels from six such decompositions was collected in ether. The ether solution was filtered and evaporated; the residue furnished the pure cyanide, b. p. 132—136°/11 mm., on distillation (yield, 144 g., 65%), m. p. 49—50°, undepressed on admixture with a specimen prepared from *o*-nitrophenyl cyanide. Its acetyl derivative had m. p. 134°; Pinnow and Sämann [6] record m. p. 133°.

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[1] Borsche, Weussmann, and Fritzsche, *Ber.*, 1924, **57**, 1149.

[2] Bargellini and Turi, *Gazzetta*, 1954, **84**, 157.

[3] Etienne and Staehelin, *Bull. Soc. chim. France*, 1954, 743.

[4] Sandmeyer, *Helv. Chim. Acta*, 1919, **2**, 234; *Org. Synth.*, Coll. Vol. I, p. 327; Calvery, Noller, and Adams, *J. Amer. Chem. Soc.*, 1925, **47**, 3058.

[5] Hovorka and Sykora, *Chem. Listy*, 1938, **32**, 241.

[6] Pinnow and Sämann, *Ber.*, 1896, **29**, 631.

2-Amino-5-methylphenyl cyanide (17·6 g., 49%) was obtained similarly from 5-methylisatin 3-oxime[7] (48 g.), b. p. 150—152°/15 mm., m. p. 59—60°; Ehrlich[8] records m. p. 60—61°.

2-*Amino*-5-*chlorophenyl cyanide.* 5-Chloroisatin 3-oxime[9] (5 g.) decomposed at 250° during 15 min. The *amino-cyanide* was collected in benzene, recovered, and, on crystallisation from water, afforded needles (2 g., 52%), m. p. 96—98° (Found: C, 54·8; H, 3·4; N, 18·2. $C_7H_5N_2Cl$ requires C, 55·1; H, 3·3; N, 18·4%).

2-*Amino*-3-*cyanobenzoic acid.* 7-Carboxyisatin 3-oxime[10] (5·1 g.) furnished a sublimate when decomposed in the same way as the foregoing example. Recrystallisation of the sublimate from aqueous ethanol gave the *amino-cyanide* (0·62 g., 16%) as needles, m. p. 280—282° (Found: C, 59·3; H, 4·0; N, 17·3. $C_8H_6O_2N_2$ requires C, 59·3; H, 3·7; N, 17·3%). This compound was amphoteric and gave a positive diazo-test.

2-*Amino*-5-*nitrophenyl cyanide.* 5-Nitroisatin 3-oxime[1] (5 g.) was heated in boiling nitrobenzene (20 ml.) for 45 min. and cooled. The solid which separated, on recrystallisation from aqueous acetone, furnished the amino-cyanide (2·6 g., 66%), m. p. 205—206°, undepressed on admixture with an authentic specimen.[11]

We thank Mr. J. D. Hunt for carrying out many preparations of *o*-aminophenyl cyanide by this method.

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[7] Meyer, *Ber.*, 1883, **16**, 2261.
[8] Ehrlich, *Ber.*, 1901, **34**, 3366.
[9] Schunck and Marchlewski, *Ber.*, 1895, **28**, 539.
[10] Rupe and Guggenbühl, *Helv. Chim. Acta*, 1927, **10**, 926, who describe this oxime erroneously as isatin 2-oxime.
[11] Baudet, *Rec. Trav. chim.*, 1924, **43**, 707.