NOTES.

425. *Thermodynamic Properties of Organic Oxygen Compounds. Part III.*[1] *Formic Acid.*

By J. H. S. Green.

The thermodynamic properties of formic acid have been reviewed by Waring [2] who tabulated the functions for the monomer from 200° to 1500° K. Recent work comprises a new vibrational assignment,[3] an accurate measurement of the heat of combustion of the liquid,[4] and new values for the dimensions of the molecule determined by microwave spectroscopy.[5] Also, it is now known that the crystal has an infinite-chain type structure [6] so that the entropy does not contain a term $\frac{1}{2}R$ ln 2 arising from random orientation. A recalculation of the thermodynamic functions has therefore been made to obtain values of improved accuracy.

[1] Part II, preceding paper.
[2] Waring, *Chem. Rev.*, 1952, **51**, 171.
[3] Millikan and Pitzer, *J. Chem. Phys.*, 1957, **27**, 1305.
[4] Sinke, *J. Phys. Chem.*, 1959, **63**, 2063.
[5] Kwei and Curl, *J. Chem. Phys.*, 1960, **32**, 1592, and references therein.
[6] Holtzberg, Post, and Fankuchen, *Acta Cryst.*, 1953, **6**, 127.

The molal thermodynamic properties of formic acid monomer in the ideal-gas state.

T (°K)	$-(G° - H_0°)/T$ (cal./deg.)	$(H° - H_0°)/T$ (cal./deg.)	$(H° - H_0°)$ (kcal.)	$S°$ (cal./deg.)	$C_p°$ (cal./deg.)	$-\Delta H_f°$ (kcal.)	$-\Delta G_f°$ (kcal.)	$\log_{10} K$
200	47·381	8·155	1·621	55·536	8·963	89·96	85·87	93·83
273·16	49·987	8·546	2·324	58·532	10·304	90·36	84·44	67·56
298·16	50·732	8·714	2·598	59·446	10·807	90·49	83·89	61·49
300	50·786	8·727	2·618	59·513	10·843	90·50	83·85	61·08
400	53·401	9·509	3·804	62·910	12·845	90·96	81·56	44·56
500	55·621	10·358	5·179	65·972	14·619	91·34	79·16	34·60
600	57·576	11·197	6·718	68·773	16·019	91·63	76·70	27·94
700	59·362	11·986	8·390	71·349	17·322	91·86	74·20	23·31
800	61·011	12·719	10·175	73·729	18·345	92·04	71·65	19·57
900	62·548	13·393	12·054	75·941	19·205	92·17	69·10	16·78
1000	63·993	14·014	14·014	78·007	19·948	92·26	66·53	14·54

Values available for the individual principal moments of inertia differ somewhat, but the values for their product required for the present purpose are in satisfactory agreement; the value $6·224 \times 10^{-116}$ g.[3] cm.[6] calculated from the results of Kwei and Curl [5] was used. The symmetry number is unity and the molecular weight was taken as 46·026. The vibrational fundamentals were taken as 3570, 2943, 1770, 1387, 1229, 1105, 1033, and 636 (2) cm.$^{-1}$ and the corresponding contributions to the thermodynamic functions were obtained by using tables.[7] Fundamental constants and other values required were those used previously.[1]

From the heat of combustion of the liquid acid,[4] the heat of vaporization,[2] and the enthalpy change on passing from the saturated vapour to the ideal-gas monomer,[2] the heat of formation of the ideal-gas monomer at 298·16° K is found to be −90·49 kcal./mole. From the statistical calculations $\Delta(H° - H_0°)_f$ is −1·75 kcal./mole at 298·16° K; therefore $\Delta H_0°_f$ is −88·74 kcal./mole. The entropy for the ideal-gas monomer at 298·16° K calculated here (59·45 cal./deg. mole) is to be compared with a value 59·44 cal./deg. mole derived [2,3] from experimental data. With the present values for the ideal-gas monomer, the following revised values for the ideal-gas dimer can be derived:

T (°K)	$-\Delta H_f°$ (kcal./92·052 g.)	$S°$ (cal./92·052 g.)	$-\Delta G_f°$ (kcal./92·052 g.)
298·16	195·12	82·89	171·19
300	195·14	83·05	171·05
400	196·21	88·48	162·86

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[*Received, November 4th*, 1960.]

[7] Johnston, Savedoff, and Belzer, " Contributions to the Thermodynamic Functions by a Planck-Einstein Oscillator in One Degree of Freedom," Office of Naval Research, Department of the Navy, Washington, D.C., 1949.

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426. *Heterocyclic Compounds of Chalcone Type.*

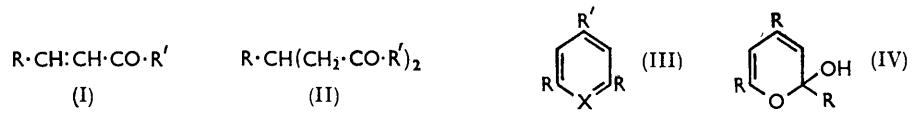
By Z. S. ARIYAN and H. SUSCHITZKY.

A NUMBER of compounds of chalcone type but containing a heterocyclic ring (I; R or R′ = heterocyclic) were prepared for biological studies. In a modification of an established method [1] ethanolic sodium hydroxide was added to a hot aqueous emulsion of the heterocyclic aldehyde and *p*-nitroacetophenone. With heterocyclic ketones as one of the reactants this procedure was satisfactory only when heating was omitted. When an excess of ketone was used and the reaction temperature was low the principal product was a Michael adduct, except in the condensation of 2-formylquinoline with acetophenone, which gave the aldol (m. p. 116°) under all conditions.[2]

Two of the Michael adducts (II; R = R′ = Ph and R = *p*-MeO·C_6H_4, R′ = Ph) were

[1] Kohler and Chadwell, *Org. Synth.*, 1922, **2**, 1.
[2] Kwartler and Lindwall, *J. Amer. Chem. Soc.*, 1937, **59**, 524.

treated with polyphosphoric acid in an attempt to cyclise them to pyrylium structures (III; X = O^+). When a solution of 1,3,5-triphenylpentane-1,5-dione (II; R = R′ = Ph)



was heated to 50° in this reagent, the mixture developed an intense green fluorescence, characteristic of the presence of pyrylium salts.[3] Neutralisation of the mixture with ammonia produced the triphenylpyridine (III; R = R′ = Ph, X = N), a result confirming the presence of a pyrylium cation which is known to be readily converted into the corresponding pyridine by ammonia or its substitution products.[4] Use of sodium hydroxide led to the triphenylpyranol (IV; R = Ph) whose infrared spectrum, in accordance with its chemical properties,[3] showed a strong carbonyl bond. Bauer[5] had obtained an unidentified substance, m. p. 137°, by the action of sodamide on the diketone (II; R = R′ = Ph); repeating this reaction we identified this compound as our triphenylpyridine. Polyphosphoric acid also proved a good cyclising agent for the preparation of the pyridine (III; R = Ph, R′ = *p*-MeO·C_6H_4, X = N).

The " chalcones " and Michael compounds showed some activity as contact poisons for the grain weevil (*Calandra granaria* L.).

TABLE 1. *Products*, R·CH:CH·CO·R′.

			Found (%)			Required (%)		Yield
R	R′	M. p.	C	H	Formula	C	H	(%)
4-Quinolyl	*p*-NO_2·C_6H_4	206°	70·9	4·0	$C_{18}H_{12}N_2O_3$	71·1	4·0	81
2-Quinolyl	,,	185·5	71·4	4·1	,,	71·1	4·0	85
2-Quinolyl	*p*-NH_2·C_6H_4	172	78·5	5·1	$C_{18}H_{14}N_2O$	78·8	5·1	74
2-Pyridyl	*p*-NO_2·C_6H_4	148·5	66·2	4·0	$C_{14}H_{10}N_2O_3$	66·1	4·2	89
4-Pyridyl	,,	216	66·5	3·6	$C_{14}H_{10}N_2O_3$	66·2	3·9	86·6
2-Furyl	,,	150	64·3	3·5	$C_{13}H_9NO_4$	64·1	3·7	89
m-NO_2·C_6H_4	2-Furyl	185	63·8	3·5	$C_{13}H_9NO_4$	64·2	3·7	92
,,	2-Thienyl	151	60·0	3·2	$C_{13}H_9NO_3S$	60·3	3·5	93
3,4-CH_2O_2:C_6H_3	*p*-NO_2·C_6H_4	210	64·6	3·7	$C_{16}H_{11}NO_5$	65·0	3·7	70
2-Quinolyl	*p*-MeO·C_6H_4	133[a]	—	—	—	—	—	69

[a] Gilman and Cason, *J. Amer. Chem. Soc.*, 1950, **72**, 3469, record m. p. 133—134°.

Experimental.—General method for preparation of chalcones. (*a*) To a vigorously stirred suspension of the appropriate aldehyde (0·1 mol.) and ketone (0·1 mol.) in water (150 ml.), heated over a small flame, about 2 ml. of 2 : 1 aqueous-ethanolic 6% sodium hydroxide solution were added. Heating was continued until a precipitate appeared. This was filtered off and yielded the *product* on recrystallisation from ethanol.

(*b*) Various *products* (I) derived from heterocyclic ketones were prepared as above, but at room temperature, and are listed in Table 1.

Preparation of Michael adducts. These *compounds* (see Table 2) were made by condensing the appropriate aldehyde (1 mol.) with the ketone (2 mol.) at room temperature under conditions described above.

Polyphosphoric acid cyclisations. (*a*) A mixture of 1,3,5-triphenylpentane-1,5-dione (1 g.) and tetraphosphoric acid (15 g.) was kept at 50° for 9 hr. with vigorous stirring. After a short time the mixture displayed an intensely green fluorescence in ultraviolet light. On pouring it into water a precipitate of 1,3,5-triphenylpyrylium phosphate was obtained. This was filtered off and triturated with aqueous ammonia, yielding 2,4,6-triphenylpyridine, m. p. 137° (from ethanol) (64%) (Found: C, 89·6; H, 5·4; N, 4·5. Calc. for $C_{23}H_{17}N$: C, 89·8; H, 5·5; N, 4·6%). Dilthey [3] reports m. p. 138·5°.

[3] Dilthey, *J. prakt. Chem.*, 1917, **95**, 107.
[4] Wislicenus and Newmann, *Annalen*, 1898, **302**, 191.
[5] Bauer, *Compt. rend.*, 1914, **158**, 1680.

TABLE 2. *Michael adducts* $R{\cdot}CH(CH_2{\cdot}CO{\cdot}R')_2$.

R	R′	M. p.	Found (%) C	Found (%) H	Formula	Required (%) C	Required (%) H	Yield (%)
4-Quinolyl	2-Naphthyl	162°	85·1	5·2	$C_{34}H_{25}NO_2$	85·2	5·3	61
4-Quinolyl	2-Thienyl	144	67·0	4·5	$C_{22}H_{17}NO_2S_2$	67·5	4·4	79
4-Quinolyl	Ph [2]	142	—	—	—	—	—	79
4-Pyridyl	Ph	120 [a]	—	—	—	—	—	87
Ph	Ph	85 [b]	—	—	—	—	—	84
3,4-CH_2O_2·C_6H_3	Ph	120	77·7	5·5	$C_{24}H_{20}O_4$	77·4	5·4	76
p-MeO·C_6H_4	Ph [c]	94	—	—	—	—	—	71

[a] Marvel, Coleman, and Scott (*J. Org. Chem.*, 1955, **20**, 1785) give m. p. 119—121°. [b,c] Kostanecki and Rossbach (*Ber.*, 1896, **29**, 1493) give (*b*) m. p. 85° and (*c*) m. p. 94 and 105°.

(*b*) When 3-*p*-methoxyphenyl-1,5-diphenylpentane-1,5-dione was treated with tetraphosphoric acid and the mixture worked up as in (*a*), 4-*p*-methoxyphenyl-2,6-diphenylpyridine, m. p. 100° (43%), was obtained (Found: C, 85·7; H, 5·7; N, 3·9. Calc. for $C_{24}H_{19}NO$: C, 85·4; H, 5·6; N, 4·1%). Dilthey *et al.*[6] record m. p. 100—101°.

We thank Mr. H. Feldman, B.Sc., of the Biology Department, the Polytechnic, Regent Street, London, for help with insecticidal experiments and Messrs. Albright and Wilson for a gift of tetraphosphoric acid.

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ROYAL MILITARY COLLEGE OF SCIENCE,
SHRIVENHAM, WILTS.

[*Received, October 18th*, 1960.]

[6] Dilthey *et al.*, *J. prakt. Chem.*, 1921, **102**, 209.

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427. *Stability Constants of Some Metal Complexes of* ortho-*Aminophenols.*

By D. D. PERRIN.

STABILITY constants of metal complexes with a wide range of ligands conform to the pattern [1,2]

$$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$$

Known exceptions, attributed to steric effects or to low-spin electronic configurations, are rare. Recently, however, the following stability constants (log K_1 at 20°, $I \sim 0{\cdot}003$) have been reported for some 1 : 1 metal complexes with 3-hydroxyanthranilic acid and *o*-aminophenol: [3]

	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
3-Hydroxyanthranilic acid	3·4	7·7	4·4	5·1	—
o-Aminophenol	3·6	8·0	4·7	5·4	8·8

Values for the 1 : 1 ferrous complexes are much higher than would be expected from the other members of the series. These anomalies, if real, would be of considerable theoretical interest; but, as it was also suggested [3] that oxidation of ferrous to ferric ion may have occurred, it was necessary to try to confirm these observations by repeating and extending some of the measurements, taking rigorous precautions to exclude oxygen.

This has now been done, and the results are tabulated. Stability constants, K_1 and

[1] Mellor and Maley, *Nature*, 1948, **161**, 436.
[2] Irving and Williams, *Nature*, 1948, **162**, 146; *J.*, 1953, 3192.
[3] Sims, *J.*, 1959, 3648.

β_2, for complex formation between metal ion and *o*-aminophenol anion were evaluated graphically [4] from the equation

$$K_1 = \frac{\bar{n}}{(1 - \bar{n})[L^-]} - \beta_2\left(\frac{2 - \bar{n}}{1 - \bar{n}}\right)[L^-] \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

values of $\bar{n}$ and $[L^-]$ derived from potentiometric titrations being used. The pK_a values of the aminophenols at the ionic strengths listed in Table 2 and used in calculating the anion concentration, $[L^-]$, were obtained from Table 1 by means of the equation

$$(pK_a)_{\mu=0} = pK_a - \tfrac{1}{2}(2x - 1)[I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) - 0{\cdot}20I] \quad . \quad . \quad . \quad . \quad (2)$$

for the equilibrium $H_nL^{x+} = H^+ + H_{n-1}L^{(x-1)+}$. This equation is derived from one due to Davies [5] and, except for 4-amino-5-hydroxynaphthalene-2,7-disulphonic acid and the higher pK_a of 3-amino-4-hydroxybenzenesulphonic acid, gives, in the present instance, essentially the same values as the limiting Debye–Hückel relation.

At the same ionic strengths, the present pK_a values and the results reported by Sims [3] for 3-hydroxyanthranilic acid and *o*-aminophenol agree to within 0·02 pH unit, and our stability constants, obtained under comparable conditions, for the 1 : 1 and the 1 : 2 copper complexes with *o*-aminophenol are also the same within experimental error. Our log K_1 values for the 1 : 1 ferrous complexes with 3-hydroxyanthranilic acid and *o*-aminophenol might have been expected to agree closely, except that for the latter the slight differences in ionic strength could introduce a difference of up to ~0·05. However, the present results are much lower that those previously reported and, in fact, they now fall into their predicted places in the Irving–Williams series. This sequence is also followed for the 1 : 1 complexes with 4-amino-5-hydroxynaphthalene-2,7-disulphonic acid. All the solutions containing ferrous complexes were very rapidly oxidised when air was admitted, and there seems little doubt that the previously-reported high stability constants were due to the presence of ferric ion.

In 1 : 1 metal complexes of 3-hydroxyanthranilic acid, steric requirements limit possible complex formation, so that the phenolic and carboxylic groups cannot bind simultaneously. However, there is probably little tendency for chelate ring formation involving the amino- and the carboxyl groups: when 0·01M-anthranilic acid in 0·02M-hydrochloric acid solution at 20° was titrated with alkali almost the same titration curves were obtained over the pH range 3·5—6·3 (being 1·4 pH units either side of the concentration-pK of 4·923) in the presence or absence of 0·005M-ferrous perchlorate.

For the ferrous complexes of 4-amino-5-hydroxynaphthalene-2,7-disulphonic acid, log K_2 exceeds log K_1 and is about 1—1·5 logarithmic units greater than would be expected from results for the corresponding cobalt, nickel, and copper complexes. The 1 : 2 ferrous complex of 3-hydroxyanthranilic acid also shows increased stability. If these results indicate that spin-pairing occurs in the 1 : 2 complexes, conditions must be near-borderline because neither the 2-aminophenol nor the 8-hydroxyquinoline [6] ferrous complex shows this effect.

Stability constants of the *o*-aminophenol ferric complexes could not be obtained by using an oxidation–reduction potential technique; [7] the system was unstable and potentials did not remain constant.

Experimental.—3-Hydroxyanthranilic acid was prepared and purified as described by Hegedüs.[8] 2-Aminophenol (prepared by catalytic hydrogenation of *o*-nitrophenol), 3-amino-4-hydroxybenzenesulphonic acid, and 4-amino-5-hydroxynaphthalene-2,7-disulphonic acid

[4] Irving and Rossotti, *J.*, 1953, 3397.
[5] Davies, *J.*, 1938, 2093.
[6] Albert, *Biochem. J.*, 1953, **54**, 646.
[7] Perrin, *J.*, 1958, 3120.
[8] Hegedüs, *Helv. Chim. Acta*, 1951, **34**, 611.

TABLE 1. *Dissociation constants (in terms of* pK_a*) of o-aminophenols at* 20°.

	Concn. (M)	pK_a (av. I)	$(pK_a)^*_{\mu=0}$
o-Aminophenol (hydrochloride)	0·005	4·816 (0·005), 9·932 (0·005)	4·781, 9·967
3-Amino-4-hydroxybenzenesulphonic acid	0·005	4·096 (0·0025), 9·052 (0·0075)	4·121, 9·146
3-Hydroxyanthranilic acid	0·001	5·181 (0·0005), 10·074 (0·0015)	5·192, 10·118
4-Amino-5-hydroxynaphthalene-2,7-disulphonic acid (monosodium salt)	0·001	3·577 (0·002), 8·703 (0·0045)	3·627, 8·827

* By extrapolation, using eqn. (2).

TABLE 2. *Stability constants of metal complexes of* o-*aminophenols at* 20°.

	Concn. (M)	Metal, concn. (M)	Max. $\bar{n}$ *	Init. I	log K_1	log β_2
o-Aminophenol (hydrochloride)	0·005	Fe^{2+}, 0·00025	0·9	0·006	3·66	6·34
	0·005	Fe^{2+}, 0·001	0·5	0·009	3·64	
	0·001	Cu^{2+}, 0·0004	0·9	0·002	8·77	16·14
3-Amino-4-hydroxybenzenesulphonic acid	0·005	Fe^{2+}, 0·001	1·15	0·009	3·32	6·13
3-Hydroxyanthranilic acid	0·001	Fe^{2+}, 0·00025	0·75	0·002	3·8	8·3
4-Amino-5-hydroxynaphthalene-2,7-disulphonic acid (monosodium salt)	0·005	Mn^{2+}, 0·002	0·3	0·021	2·18	
	0·005	Fe^{2+}, 0·001	0·5	0·018	2·57	5·5
	0·005	Co^{2+}, 0·002	0·6	0·021	2·84	4·4
	0·005	Ni^{2+}, 0·002	1·05	0·021	3·47	5·26
	0·005	Cu^{2+}, 0·0016	2	0·020	6·91	11·15
	0·005	Zn^{2+}, 0·0005	0·2	0·016	2·45	

* Graph of $\bar{n}/(1-\bar{n})[L^-]$ against $(2-\bar{n})[L^-]/1-\bar{n})$ linear up to this value. Except for copper plus aminohydroxynaphthalenedisulphonic acid, precipitation occurred at slightly greater values of $\bar{n}$.

(monosodium salt) were purified by repeated recrystallisation from water, under nitrogen, and vacuum-dried. The metal ions were added as the perchlorates prepared by ion-exchange [9] or by double decomposition (Fe^{2+}).[7]

All pH measurements were made at 20° by using the apparatus and technique described previously,[9] except that the Perspex stopper was replaced by a tightly fitting soft rubber one. Details of titrations are summarised in the Tables. The agreement of results for *o*-aminophenol with two different concentrations of ferrous ion suggests that there was no appreciable polynuclear complex formation. Constants given to two decimal places are probably accurate to within ±0·05. Dissociation constants have been calculated from the hydrogen-ion activity as measured by the glass electrode, the complete Henderson–Hasselbach equation being used.

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[9] Perrin, *J.*, 1960, 3189.

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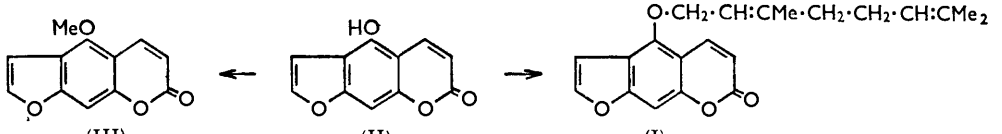
428. *The Synthesis of Bergamottin.*

By A. CHATTERJEE and (MISS) B. CHAUDHURY.

BERGAMOTTIN, 5-geranyloxypsoralene, was isolated by Späth and Kainrath [1] in 1937 from bergamot oil occurring in *Citrus bergamia* Risso (Fam. Rutaceae). Though there has



(III) (II) (I)

been little doubt that it has structure [1] (I), yet during the intervening twenty-three years no synthesis has been reported. We have now accomplished this.

[1] Späth and Kainrath, *Ber.*, 1937, **70**, 2272.

Bergaptol (II), prepared by Späth and Kubiczek's method [2] or from bergapten (III) by demethylation,[3] was refluxed for 80 hr. in alcohol with geranyl chloride [4] and sodium ethoxide, giving a 10% yield of bergamottin. The latter was isolated with great difficulty from the dark brown reaction product as, particularly when impure, it is extremely thermolabile and sensitive to acids, which caused complete resinification of the substance. A suitable procedure was, however, developed.

Experimental.—Metallic sodium (0·50 g.) was dissolved in absolute ethanol (85 ml.), and geranyl chloride (3·0 g.) and bergaptol (2·05 g.) were slowly added with cooling. The mixture was then heated under reflux for 80 hr. The solution was then cooled in ice, covered with ether (200 ml.), diluted with water (500 ml.), and shaken vigorously. Extraction with ether was repeated (3 × 50 ml.) and the total ether extract was washed with 5% aqueous alkali (3 × 30 ml.) to remove bergaptol, dried, and concentrated. The concentrate was chromatographed over Alcoa alumina, light petroleum (b. p. 60—80°) and ether being used as eluants and fractions of 25 ml. being collected. Fractions 1—8 (light petroleum, b. p. 60—80°) yielded a liquid (0·50 g.) with a smell of geraniol. Fractions 8—10 (ether) gave a semisolid mass (0·54 g.) on evaporation. This was rechromatographed over Alcoa alumina and eluted with light petroleum (b. p. 60—80°) and ether. The ether eluates afforded a colourless wax (0·46 g.) that was dissolved in light petroleum (b. p. 60—80°) (2 ml.) and kept at 0° for a few days; crystals (0·1 g.) appeared, which after several crystallisations from ethanol formed stout rods, m. p. 60° (Found: C, 74·48; H, 6·49. Calc. for $C_{21}H_{22}O_4$: C, 74·55; H, 6·5%), $\lambda_{max.}$ 220 (log ε 4·41), 250 (log ε 4·28), and 309 mμ (log ε 4·17), $\nu_{max.}$ (in Nujol) 5·82 (lactone), 6·24 (C=C), 6·33 (Ph), 7·39—7·55 (multiple peak, gem.-Me_2), 8·31 (Ph ether), 9·37 (furan), and 12·13 μ (trisubstituted double bond).

This product did not depress the m. p. of bergamottin prepared from bergamot oil, obtained through the courtesy of S. B. Pencick & Co., U.S.A., which had the same infrared and ultraviolet absorption. Our bergamottin was hydrolysed in acid, as was the natural coumarin, to bergaptol (II) and geraniol, these being respectively characterised as bergapten (III), m. p. 190°, and the allophanate, m. p. 124°. Bergaptol was also obtained from synthetic bergamottin by thermal decomposition.

The authors thank Mr. B. B. Bhattacharya, University College of Science, for microanalyses.

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[2] Späth and Kubiczek, *Ber.*, 1937, **70**, 1253.
[3] Schönberg and Aziz, *J. Amer. Chem. Soc.*, 1955, **77**, 2563.
[4] Forster and Cardwell, *J.*, 1913, **103**, 1341.

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429. *Nitromethane: Second Virial Coefficients.*

By G. A. Bottomley and I. H. Coopes.

With the type of very accurate compressibility apparatus used previously [1] for organic vapours, nitromethane (b. p. 101°) has been examined at 50°/42—95 mm. and at 67°/66—210 mm.; and gives for B^* in the equation $PV = RT + B^*P$ [where P is the pressure (atm.), V the volume (cm.^{3}) occupied by 1 mole, and T the absolute temperature] the values of −2926 and −2317 cm.^{3}/mole respectively.

Experimental.—Material. Nitromethane was synthesised [2] from chloroacetic acid and sodium nitrite, refluxed in a stream of nitrogen, and dried over boric acid previously dehydrated in a vacuum at 200°. It was difficult to obtain nitromethane for which the Young's device [1a]

[1] (*a*) Bottomley, Reeves, and Whytlaw-Gray, *Proc. Roy. Soc.*, 1958, *A*, **246**, 504; (*b*) Bottomley and Reeves, *J.*, 1958, 3794.
[2] Vogel, "A Text-book of Practical Organic Chemistry," Longmans, Green and Co. Ltd., London, 1954, p. 306.

indicated satisfactory " de-gassing "; additional gas accumulated during storage in the " Phœnix "-glass preparation lines which were controlled solely by mercury " cut-offs."

Stability. Freshly purified nitromethane was tested in the compressibility apparatus by determining daily the pressure–volume product at constant pressure. At 50° the quantity of gas increased by some 4 parts per 100,000 per day (rather more initially, rather less after some days). The rate of increase was smaller at lower pressures and greater at 67°. No fouling of the glass or the grease-free mercury surfaces could be detected visually. Some photochemical influence was demonstrated. Excessively frequent redeterminations of the pressure–volume product definitely enhanced the volume increase.

Conduct of PV measurement. We have obtained the quoted compressibility results by following quantitatively the slight decomposition for some days, expanding the vapour to a new pressure, repeating the quantity–time determinations, and extrapolating both series of PV's to the time of expansion. The technique is otherwise as previously reported and the normal precision of 1 in 100,000 on the PV's is retained. The unknown decomposition products present to much less than 0·1% cannot significantly disturb the virial determinations.

Discussion.—Static electricity. We attribute most of the decomposition to static electricity generated by mercury movement over the dry glass surfaces both during the manipulations and inadvertently through minor vibrations in the laboratory. The instability, which corresponds to a first-order half-reaction time of about 15 years, is similar to that of carbon tetrachloride.[1b]

Adsorption. Separate determinations of the vapour adsorption on glass have been made by improved versions of the method previously described [3] and the observed PV values are appropriately corrected. The corrections for adsorption on the mercury surfaces are more difficult because of the paucity of suitable data. Cassel and Salditt [4] report for nitromethane values at 50° derived from the change in surface tension of mercury, but Kemball and Rideal [5] produce evidence that Cassel and Salditt's mercury was contaminated by non-polar materials. We have supposed provisionally that the adsorption (moles/cm.^{2}) on the mercury is twice that on the glass as for benzene vapour. At 67° the adsorption corrections, which are the greatest uncertainty in the experiments, cannot affect the B^* value by more than ± 3 cm.^{3}/mole at most: at 50° the effects are more serious, but certainly less than ± 10 cm.^{3}/mole.

Comparison with other values. McCullough and his co-workers [6] published data on the vapour pressure, latent heat of vaporisation, and vapour heat-capacity of nitromethane which Douslin and Waddington [7] correlated by means of a Stockmayer intermolecular potential. For comparison with Douslin and Waddington's work we have re-cast our results in terms of $PV = \boldsymbol{R}T + B/V$, which makes $B = -2866$ (50°) and -2247 (67°) cm.^{3}/mole. We have used a $\log_{10} B$–$1/T$ plot (which is linear except at the lowest temperature) to interpolate their virial coefficient values to our temperatures and estimate that our B values are less negative by 2·2% (50°) and 1·3% (67°).

The extremely high non-ideality of nitromethane vapour and other physical properties, which are often attributed to association, make desirable a careful examination of the PV–P curve for indications of abnormal non-linearity. It is most regrettable that the observed instability hinders this work.

Department of Chemistry, The University of Western Australia,
Nedlands, Western Australia. [*Received, November 21st*, 1960.]

[3] Bottomley and Reeves, *Trans. Faraday Soc.*, 1957, **53**, 1455.
[4] Cassel and Salditt, *Z. phys. Chem.* (*Leipzig*), 1931, **155**, 321.
[5] Kemball and Rideal, *Proc. Roy. Soc.*, 1946, *A*, **187**, 53.
[6] McCullough, Scott, Pennington, Hossenlopp, and Waddington, *J. Amer. Chem. Soc.*, 1954, **76**, 4791.
[7] Douslin and Waddington, *J. Chem. Phys.*, 1955, **23**, 2453.

430. *A New Stereospecific Reaction.*

By H. Irving and R. D. Gillard.

It has been shown that the following reactions between (*a*) complexes of ethylenediaminetetra-acetic acid (edta) or (+)-propylenediaminetetra-acetic acid, $A_2N{\cdot}CHMe{\cdot}CH_2{\cdot}NA_2$ (pdta; A = $CH_2{\cdot}CO_2H$) with cobalt(III), and (*b*) ethylenediamine (en) or (±)-propylenediamine (pn), occur with increasing retention of configuration: *

(+)-$[Co(edta)]^-$ + en = (+)-$[Co(en)_3]^{3+}$ + edta (ref. 1)
(+)-$[Co(edta)]^-$ + (±)-pn = (+)-$[Co(+\text{-}pn)_3]^{3+}$ + edta (ref. 2)
(−)-$[Co(+\text{-}pdta)]^-$ + (±)-pn = (+)-$[Co(+\text{-}pn)_3]^{3+}$ + (+)-pdta (ref. 3)

It has now been shown that the reaction:

(−)-$[Co(+\text{-}pdta)]^-$ + en = (+)-$[Co(en_3)]^{3+}$ + (+)-pdta

proceeds at 25° with a retention of configuration comparable with that of reaction (2) above: the pdta displaced from the complex anion retains its full optical activity.

Experimental.—Ethylenediamine (0·8 g., 0·0132 mole) in water (3 ml.) was added to a solution of lævorotatory potassium (+)-1,2-propylenediaminetetra-acetatocobalt(III) trihydrate (1 g., 0·0022 mole) in water (5 ml.) at 20°. During 12 min. at 25·0° the originally deep purple mixture became orange. After a further 15 min. sodium iodide (1 g.) in water (1 ml.) was added and the whole poured into ice-cold acetone (150 ml.). A viscous orange mass (A) separated and the mother-liquor (B) was removed by decantation. The product (A) was taken up in water (2 ml.) and poured into ice-cold acetone (100 ml.); a viscous orange material again separated. After removal of the supernatant liquid this was thoroughly cooled; scratching then caused separation of dextrorotatory trisethylenediamminocobalt(III) iodide trihydrate as a yellow powder (1·33 g., 90%) (Found: Co, 8·7. Calc. for $C_6H_{24}N_6I_3,3H_2O$: Co, 8·74%). In water $[M]_D^{20}$ = +537°. Werner [4] gives +602·5° and +552·5° for the corresponding bromide and chloride.

The acetone mother-liquors (B) were concentrated to 30 ml. on a water-bath, acidified to pH 2 with dilute hydrochloric acid, and passed through a column of cation-exchange resin (ZeoKarb 225, H^+ form). The effluent was concentrated to 5 ml. and strongly cooled; scratching caused the separation of (+)-pdta monohydrate as a white powder (0·55 g., 77%) with $[\alpha]_D^{20}$ +46°. Dwyer and Garvan [5] report +47°. After being dried at 130° the anhydrous material had m. p. 193° and $[\alpha]_D^{20}$ +50°. Dwyer and Garvan [5] report m. p. 194° and the same rotation.

We thank Mr. Ridley for the polarimetric measurements.

Inorganic Chemistry Laboratory, Oxford. [*Received, November 21st,* 1960.]

* (+) and (−) outside the square bracket refer to the whole ion.

[1] Dywer, Gyarfas, and Mellor, *J. Phys. Chem.*, 1955, **59**, 296.
[2] Bailar, Kirschner, and Yung Kang Wei, *J. Amer. Chem. Soc.*, 1957, **79**, 5877.
[3] Irving and Gillard, *J.*, 1960, 5266.
[4] Werner, *Ber.*, 1912, **45**, 124.
[5] Dwyer and Garvan, *J. Amer. Chem. Soc.*, 1959, **81**, 2955.

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431. 10-*Methylphenanthridine.*

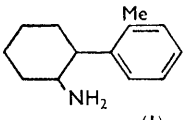
By M. S. Gibson.

10-Methylphenanthridine, whose picrate was required as a reference compound, has been prepared by application of the Diels–Alder and Bischler–Napieralski reactions.

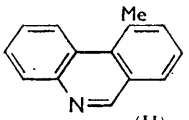
o-Tolualdehyde was condensed with nitromethane to give 2-methyl-ω-nitrostyrene. The Diels–Alder adduct [1] from the latter and butadiene was then hydrogenated to the

[1] Cf. Allen, Bell, and Gates, *J. Org. Chem.*, 1943, **8**, 373.

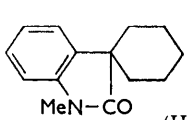
intermediate cyclohexylamine (I). Formylation and dehydration gave 1,2,3,4,4a,10b-hexahydro-10-methylphenanthridine (*ca.* 5% yield), which was dehydrogenated by selenium [2] to the phenanthridine (II), which was isolated as the picrate.



(I)



(II)



(III)

The oxindole (III) has been prepared from cyclohexanecarboxylic acid and *N*-methyl-*N*-phenylhydrazine by Brunner's method.[3] The speculation that distillation with zinc dust might yield phenanthridine was not realized; nor did dehydrogenation give basic products.

Experimental.—*2-Methyl-ω-nitrostyrene.* Sodium hydroxide (7 g.) in water (18 ml.) was added dropwise to a stirred solution of *o*-tolualdehyde (20 g.) and nitromethane (10 g.) in methanol (35 ml.), the mixture being kept at 10—15°. As the mixture became pasty, methanol (15 ml.) was added. Stirring was continued for a further 15 min., and then ice and water (*ca.* 300 g.) were added. The resulting solution was added to 14% hydrochloric acid (90 ml.), a yellow oil separating. Ether-extraction, drying, and distillation gave *2-methyl-ω-nitrostyrene* (19 g.), b. p. 150—151°/13 mm., n_D^{14} 1·6276 (Found: C, 66·3; H, 5·5; N, 8·7. $C_9H_9NO_2$ requires C, 66·3; H, 5·5; N, 8·6%).

4-Nitro-5-o-tolylcyclohexene. A mixture of 2-methyl-ω-nitrostyrene (17 g.), butadiene (10 g.), and toluene (24 ml.) was heated in an autoclave for 5 hr. at 150°. Evaporation *in vacuo* gave a dark oil, which solidified on trituration with light petroleum. Crystallisation from aqueous methanol (charcoal) gave *4-nitro-5-o-tolylcyclohexene* (16 g.) as brownish needles, m. p. 65—71°, raised after two further crystallisations to 79—80° (Found: C, 72·2; H, 7·15; N, 6·25. $C_{13}H_{15}NO_2$ requires C, 71·9; H, 6·9; N, 6·45%).

4-Methyl-ω-nitrostyrene [4] (3·1 g.) similarly gave *4-nitro-5-p-tolylcyclohexene* (2·8 g.; 1·8 g. after four crystallisations with charcoal), which formed elongated plates, m. p. 84—86°, from aqueous methanol (Found: C, 71·6; H, 7·0; N, 6·5%).

2-o-Tolylcyclohexylamine. 4-Nitro-5-*o*-tolylcyclohexene (10 g.) was hydrogenated in warm ethanol over Raney nickel at atmospheric pressure (absorption 4·27 l.). The catalyst was filtered off, and the filtrate concentrated *in vacuo*. The resulting oil was dissolved in dry benzene and saturated with dry hydrogen chloride. Evaporation *in vacuo* gave a gummy solid. This was leached with boiling water (charcoal), and the filtrate was basified and extracted with ether. Drying and saturation with dry hydrogen chloride precipitated the *hydrochloride* as a colourless solid. The salt (7·8 g.) separated from ether–ethanol as prisms, m. p. 228—229° (Found: C, 69·4; H, 8·8; N, 6·5. $C_{13}H_{20}NCl$ requires C, 69·2; H, 8·9; N, 6·2%). Addition of aqueous sodium nitroprusside solution, followed by a few drops of sodium carbonate solution, to the hydrochloride in aqueous acetone, produces a plum-red colour which slowly becomes purple.

1,2,3,4,4a,10b-Hexahydro-10-methylphenanthridine picrate. 2-*o*-Tolylcyclohexylamine (from 7·5 g. of hydrochloride) was heated with 98—100% formic acid (2·5 ml.) at 150° for 5 hr. in an open flask. The crude formyl derivative was dissolved in purified tetralin (125 ml.), and phosphoric anhydride (18 g.) was added to the boiling solution during 40 min. The tetralin was then decanted, and the brown residue was washed with ether and extracted with hot aqueous hydrochloric acid (charcoal). The acidic filtrate was washed with ether, basified, and the resulting suspension extracted with ether. Treatment of the dried ether extract with dry hydrogen chloride yielded a brown gum. This was dissolved in boiling water (charcoal), and the filtrate was basified and extracted with ether. Addition of ethanolic picric acid to the dried ether solution precipitated the *hexahydromethylphenanthridine picrate* (620 mg.). Three crystallisations from aqueous ethanol gave yellow needles, m. p. 172—173° (Found: C, 56·2; H, 4·4; N, 13·4. $C_{20}H_{20}N_4O_7$ requires C, 55·9; H, 4·7; N, 13·1%).

[2] Cf. Braude and Fawcett, *J.*, 1951, 3113.
[3] Cf. Moore and Plant, *J.*, 1951, 3475.
[4] Worrall, *J. Amer. Chem. Soc.*, 1938, **60**, 2841.

10-*Methylphenanthridine picrate*. The hexahydrophenanthridine (from 200 mg. of picrate) was heated with powdered selenium (140 mg.) at 360° for 6 hr. The dark residue was extracted with hot dilute hydrochloric acid (charcoal), and the filtrate was basified and extracted with ether. Ethanolic picric acid precipitated 10-*methylphenanthridine picrate* (65 mg.) from the dried solution. The salt separated from acetone as yellow prisms, m. p. 204—206° (Found: C, 56·5; H, 3·6; N, 13·0. $C_{20}H_{14}N_4O_7$ requires C, 56·9; H, 3·3; N, 13·3%). The free base was not characterised.

Attempted dehydrogenation at 330° with selenium led only to recovery of a small amount of the hexahydrophenanthridine picrate.

1-*Methyloxindole-3-spirocyclohexane*. A mixture of *N*-methyl-*N*-phenylhydrazine (5 g.) and cyclohexanecarboxylic acid [5] (5 g.) was heated at 165° for 3 hr., then poured into water; the *hydrazide* that separated crystallised from aqueous ethanol as needles, (8 g.), m. p. 141—142° (Found: C, 72·6; H, 8·8; N, 11·8. $C_{14}H_{20}N_2O$ requires C, 72·4; H, 8·6; N, 12·1%).

A mixture of the hydrazide (7·5 g.) with freshly baked calcium oxide (22·5 g.) was heated at 250—280° until evolution of ammonia slackened (3—4 hr.). The cooled mixture was treated with an excess of 20% hydrochloric acid, much tar separating. After 30 minutes' boiling, the mixture was cooled and extracted with ether. The *spiran* (2 g.) was obtained as a pale yellow gum, b. p. 180—182°/19 mm. (Found: C, 77·8; H, 7·8; N, 6·7. $C_{14}H_{17}ON$ requires C, 78·1; H, 7·9; N, 6·5%). It gives an intense magenta colour with concentrated sulphuric acid and a crystal of sodium dichromate.

Bromination in acetic acid gave (probably) the 5,7-*dibromo-derivative*, which crystallised from aqueous ethanol in needles, m. p. 136—137° (Found: C, 45·0; H, 3·9. $C_{14}H_{15}ONBr_2$ requires C, 45·0; H, 4·0%).

The parent oxindole distilled unchanged from zinc dust at 280—300°; dehydrogenation with sulphur produced carbonaceous material from which no basic product could be isolated.

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[*Received, November 25th*, 1960.]

[5] Sabatier and Mailhe, *Ann. Chim.* (*France*), 1907, **10**, 527.

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432. *Applications of the "Abnormal" Reimer–Tiemann Reaction.*

By M. S. GIBSON.

DETAILS of experiments which were to serve as a model for a synthesis of ferruginol are now reported.

Reaction of 4-methyl-1-naphthol with chloroform and alkali (dichlorocarbene) has been shown [1,2,3] to give 1-dichloromethyl-1,4-dihydro-1-methyl-4-oxonaphthalene. The isomeric 2-methyl-1-naphthol similarly gives [1,4,5] 1-dichloromethyl-1,2-dihydro-1-methyl-2-oxonaphthalene, though in much better yield. For the purpose of the model, 1,2,3,4-tetrahydro-1,1-dimethylphenanthr-9-ol was prepared from ethyl γ-(4-methoxy-1-naphthyl)-butyrate by reaction with methylmagnesium iodide, dehydration of the intermediate

[1] Gibson, *Experientia*, 1951, **7**, 176.
[2] Fuson and Miller, *J. Org. Chem.*, 1952, **17**, 316.
[3] Wenkert and Stephens, *J. Amer. Chem. Soc.*, 1956, **78**, 5627.
[4] Bell and Hunter, *J.*, 1950, 2903.
[5] Dodson and Webb, *J. Amer. Chem. Soc.*, 1951, **73**, 2767.

alcohol, cyclisation to the tetrahydrophenanthrene, and demethylation with hydriodic acid. This phenol reacted with dichlorocarbene to yield only the " abnormal " product:

it seems that the 1-methyl groups exert greater hindrance at position 10 than at position 4a, and the latter is thus the preferred site of attack by dichlorocarbene.

This result is interesting since the " abnormal " Reimer–Tiemann reaction has been successfully applied to *ar*-β-[6] and *ar*-α-tetralol,[7] but failed when applied to various steroid analogues (*e.g.*, œstrone), evidently because of the steric interference by axial 8-, 9-, and 11-hydrogen atoms with attack by dichlorocarbene at positions 10 and 13.

Experimental.—Most of the analyses were by Mr. F. C. Hall; ultraviolet spectra were measured for ethanol solution by Mr. F. Hastings.

Ethyl γ-(4-methoxy-1-naphthyl)butyrate.[8] A solution of γ-(4-methoxy-1-naphthyl)butyric acid [9] (20 g.) in ethanol (275 ml.) and concentrated sulphuric acid (12 ml.) was refluxed for 14 hr., giving, in the usual way, the *ethyl ester* (15 g.), b. p. 167—170°/0·18 mm., n_D^{16} 1·5703 (Found: C, 75·3; H, 7·5. $C_{17}H_{20}O_3$ requires C, 75·0; H, 7·4%).

2-Methyl-5-(4-methoxy-1-naphthyl)pentan-2-ol and dehydration thereof. Ethyl γ-(4-methoxy-1-naphthyl)butyrate (14 g.) in dry ether (50 ml.) was added during 30 min. to a boiling solution of methylmagnesium iodide (from 5 g. of magnesium) in ether (65 ml.). Boiling was continued for 6 hr. After being kept overnight, the mixture was decomposed with ice and sulphuric acid, and extracted with ether. Washing with sodium hydrogen carbonate solution and water, drying, and evaporation gave the crude alcohol as a yellow oil. Distillation gave a mixture of alcohol and olefin(s) (11 g.), collected at 129—144°/0·04 mm. (Found: C, 83·0; H, 8·6%).

The mixture (10·5 g.) was heated with anhydrous copper sulphate (3 g.) at 150—160° until no more water was evolved (1—2 hr.). When cool, water was added, and the product was isolated with ether. Distillation gave mixed 2-methyl-5-(4-methoxy-1-naphthyl)pentenes (9·5 g.), b. p. 132—137°/0·03 mm., n_D^{16} 1·5914 (Found: C, 84·9; H, 8·3. Calc. for $C_{17}H_{20}O$: C, 85·0; H, 8·3%).

On hydrogenation in acetic acid with palladised charcoal the olefins (248 mg.) absorbed 24 ml. of gas at 17°/760 mm. (0·98 double bond).

The olefins decolorised alkaline potassium permanganate solution immediately.

1,2,3,4-Tetrahydro-9-methoxy-1,1-dimethylphenanthrene. A solution of the olefins (7 g.) in dry chloroform (70 ml.) was saturated with dry boron trifluoride with ice-cooling. After 30 min., the brown solution was allowed to warm to room temperature (10—15 min.) and then poured into an excess of sodium acetate solution with stirring. The chloroform extract was washed, dried, and distilled to yield the *phenanthrene* (6 g.), b. p. 150—170° (bath)/0·06 mm. The re-distilled compound solidified on trituration with light petroleum, and separated from ether as colourless rhombs, m. p. 59° (Found: C, 84·8; H, 8·4. $C_{17}H_{20}O$ requires C, 85·0; H, 8·3%).

The product was not hydrogenated under the above conditions; nor did it decolorise potassium permanganate solution.

In a separate experiment, 100% phosphoric acid at 100° for 8 hr. effected only 30% cyclisation (calc. from hydrogenation results).

1,2,3,4-Tetrahydro-1,1-dimethylphenanthr-9-ol. A solution of 1,2,3,4-tetrahydro-9-methoxy-1,1-dimethylphenanthrene (5 g.) in acetic acid (60 ml.) and freshly distilled hydriodic acid (25 ml.; *d* 1·7) was heated at 120—130° under carbon dioxide for 3 hr. The cooled mixture was poured into water, neutralised with sodium carbonate solution, and decolorised with sodium dithionite. The precipitated *1,2,3,4-tetrahydro-1,1-dimethylphenanthr-9-ol* (4·5 g.) was collected, washed

[6] Woodward, *J. Amer. Chem. Soc.*, 1940, **62**, 1208.
[7] Wynberg and Johnson, *J. Org. Chem.*, 1959, **24**, 1424.
[8] Cf. Burtner, U.S.P. 2,590,086/1952.
[9] Martin, *J. Amer. Chem. Soc.*, 1936, **58**, 1438.

and dried. Crystallisation from cyclohexane gave prisms, m. p. 139° (Found: C, 84·7; H, 8·2. $C_{16}H_{18}O$ requires C, 84·95; H, 8·0%).

4a-*Dichloromethyl*-1,2,3,4,4a,9-*hexahydro*-1,1-*dimethyl*-9-*oxophenanthrene*. Chloroform (10 g.) was added during 3 hr. to a solution of 1,2,3,4-tetrahydro-1,1-dimethylphenanthr-9-ol (3·8 g.) in 10% aqueous sodium hydroxide (60 ml.) kept under reflux at 75°. After a further hour, the mixture was cooled, slightly acidified, and extracted with chloroform. The extract was washed with sodium hydroxide solution and water, dried, and evaporated. The residue was adsorbed on alumina from benzene–light petroleum solution; elution with benzene gave yellowish, slightly gummy fractions, which were collected in ethanol. Evaporation to small bulk and chilling gave 4a-*dichloromethyl*-1,2,3,4,4a,9-*hexahydro*-1,1-*dimethyl*-9-*oxophenanthrene* (0·5 g.), which separated from cyclohexane as plates, m. p. 124° (Found: C, 66·6; H, 5·8; Cl, 23·15. $C_{17}H_{18}Cl_2O$ requires C, 66·0; H, 5·8; Cl, 23·0%), $\lambda_{max.}$ 255 (log ε 4·06) and (sh) 279 mμ (log ε 3·91), $\lambda_{infl.}$ 270 mμ (log ε 3·96).

The alkaline washings from the extraction were acidified and extracted with chloroform. Evaporation and chromatography on silica gave starting material (0·5 g.; eluted with benzene).

1-*Dichloromethyl*-1,4-*dihydro*-1-*methyl*-4-*oxonaphthalene*. In like manner, 4-methyl-1-naphthol [10] (2 g.) gave the dichloro-ketone (0·4 g.), isolated chromatographically from neutral products. The compound separated from cyclohexane in needles, m. p. 106—107° (Found: C, 59·8; H, 4·4; Cl, 29·4. Calc. for $C_{12}H_{10}Cl_2O$: C, 59·8; H, 4·2; Cl, 29·45%), $\lambda_{max.}$ 231 (log ε 3·98) and 263 mμ (log ε 3·84), $\lambda_{min.}$ 251 mμ (log ε 3·82).

1-*Dichloromethyl*-1,2-*dihydro*-1-*methyl*-2-*oxonaphthalene*. 1-Methyl-2-naphthol (2 g.) similarly reacted with chloroform and sodium hydroxide. Chromatography of neutral products on alumina and crystallisation from light petroleum (b. p. 40—60°) gave the dichloro-ketone (2 g.) as blades, m. p. 66—67° (Found: C, 60·0; H, 4·3; Cl, 29·2. Calc. for $C_{12}H_{10}Cl_2O$: C, 58·8; H, 4·2; Cl, 29·45%), $\lambda_{max.}$ 237 (log ε 4·11) and 313 mμ (log ε 3·98), $\lambda_{min.}$ 257 mμ (log ε 2·68).

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The University, Manchester, 13. [*Received, December 6th*, 1960.]

[10] Elbs and Christ, *J. prakt. Chem.*, 1923, **106**, 17.

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433. 3-*Nitro*-2-*naphthoic Acid*.

By R. D. Topsom and J. Vaughan.

Berliner and Winicor [1] measured the dissociation constants of thirteen mononitronaphthoic acids at 25° in 50% aqueous "butyl cellosolve" (2-butoxyethanol). The remaining member of this series (3-nitro-2-naphthoic acid) could not then be prepared. This acid has now been made from 3-amino-2-naphthoic acid, *via* the diazonium sulphate, the simplified technique of Ward, Johnson, and Hawkins [2] being used. Preparation from the amino-ester was unsatisfactory because extraction of the product was difficult, and attempts to make the required acid through the diazonium fluoroborate were unsuccessful.

The pK of the acid, determined under Berliner's conditions, was 4·89 and that of 2-naphthoic acid 5·97. The difference (1·08) is smaller than that for the 1-nitro-acid ($\Delta pK = 1·42$) and is greater than that for the 4-nitro-acid ($\Delta pK = 0·98$).[1] The acidity of 3-nitro-2-naphthoic acid is thus approximately that which would be predicted following Berliner and Winicor's discussion.

Experimental.—3-*Nitro*-2-*naphthoic acid*. To a paste of 3-amino-2-naphthoic acid (7·5 g.) with water (20 ml.) were added sulphuric acid (8 ml.), water (20 ml.), and crushed ice (40 g.). Sodium nitrite solution (4·0 g. in 10 ml.) was added to the stirred mixture and stirring continued

[1] Berliner and Winicor, *J. Amer. Chem. Soc.*, 1959, **81**, 1630.
[2] Ward, Johnson, and Hawkins, *J.*, 1960, 894.

for 5 min. The mixture was then added to a hot, stirred mixture of sodium nitrate (150 g.), hydrated copper sulphate (20 g.), cuprous oxide (12 g.), and sodium hydrogen carbonate (40 g.) in water (400 ml.). Much gas was evolved and stirring was continued for 1 hr. The precipitate was filtered off and washed with saturated sodium hydrogen carbonate solution (3 × 50 ml.). The combined filtrates were cooled and carefully acidified (to pH 5) with dilute sulphuric acid before being extracted with ether (250 ml.). Addition of acid and extraction with ether were carried out twice more. The total ethereal extract was then washed twice with water and extracted with sodium hydroxide solution until colour was no longer removed. Addition of acid precipitated the crude 3-*nitro*-2-*naphthoic acid*, m. p. 211—214°, as a pale yellow solid (2·2 g.; 25% theory). The acid was purified chromatographically on alumina, ethanol being used as solvent and ethanol : water (1 : 3) as eluent. Recrystallisation from dilute ethanol gave white crystals m. p. 220·5° (Found: C, 60·9; H, 3·2; N, 6·0, 6·6. $C_{11}H_7O_4N$ requires C, 60·8; H, 3·2; N, 6·45%).

Dissociation constant. Berliner and Winicor's method was followed, a Cambridge portable pH meter being used. The purified butyl cellosolve (2-butoxyethanol) boiled at 170·5—171°/764 mm. Two determinations gave the pK of 3-nitro-2-naphthoic acid as 4·90 and 4·87. Compatibility with Berliner's results was checked with 2-naphthoic acid (pK 5·95, 5·98; in agreement with Berliner's figure, 5·95).

We thank Dr. A. D. Campbell, University of Otago, for the microanalyses.

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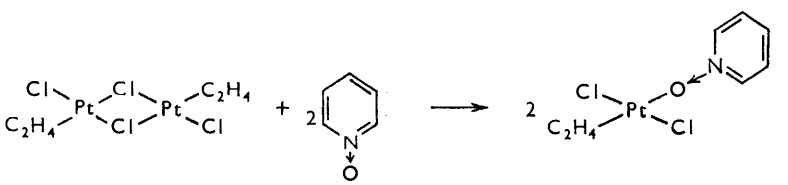
434. *Ethylene-platinous Chloride Pyridine* N-*Oxide.*

By LEONARDO GARCIA and MILTON ORCHIN.

ANDERSON has reported[1] that treatment of ethylene-platinous chloride (di-μ-chloro-dichlorodiethylenediplatinum) with an excess of pyridine results in complete displacement of all the ligands and the formation of a salt $[Pt(C_5H_5N)_4]Cl_2$. In connexion with the studies[2] on the relative strength of ligand bonding in platinum(II)–olefin complexes, a variety of pyridine compounds have been investigated.

When an aqueous solution of Zeise's salt ($K[C_2H_4PtCl_3]$) is treated with 1—4 mol., or with a large excess, of pyridine 1-oxide, the same stable compound separated on storage at room temperature; it recrystallized from chloroform as green needles, m. p. 145—146° (decomp.). The identical compound (infrared spectrum, ultimate analysis, m. p., and appearance) was secured on treatment of the non-ionic dimeric ethylene-platinous chloride $[C_2H_4PtCl_2]_2$ in ethanol with pyridine 1-oxide. In neither of the platinum complex reactions with pyridine oxide was gas evolved, and the spectrum of the product showed an absorption peak at 3000 cm.$^{-1}$ characteristic of the olefinic C–H stretching mode. Analysis of the green *compound* [Found, for material from the dimeric complex: C, 21·8;



H, 2·6; N, 3·6. Found, for material from Zeise's salt: C, 22·0; H, 2·4; N, 3·6. $(C_2H_4)PtCl_2(C_5H_5NO)$ requires C, 21·6; H, 2·3; N, 3·6%] indicates that both reactions involve straight-forward displacements which, in the case of the dimeric complex, can be written as illustrated. A similar reaction with Zeise's salt can be written, but then chloride ion is liberated.

[1] Anderson, *J.*, 1934, 1971.
[2] Joy and Orchin, *J. Amer. Chem. Soc.*, 1959, **81**, 305, 310.

Although there is no unequivocal evidence that the pyridine oxide takes up the position *trans* to ethylene, it is reasonable to expect this disposition because of the *trans*-activating effect of the unsaturated ligand. The failure to incorporate more than one pyridine oxide molecule is probably due to the weaker basicity of the oxide (pK 0·79) than of the parent pyridine [3] (pK 5·29), although there is usually little correlation between the basicity of a ligand and its tendency to form platinum complexes.

We thank the Engelhard Industries, Inc., for a generous supply of platinum.

UNIVERSITY OF CINCINNATI,
CINCINNATI, OHIO, U.S.A [*Received, November 10th*, 1960.]

[3] Jaffé and Doak, *J. Amer. Chem. Soc.*, 1955, **77**, 4441.

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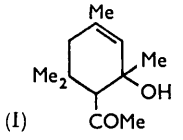
435. *Reaction Products from Mesityl Oxide and Lithium.*

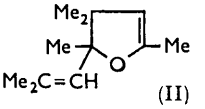
By N. BACON, S. BREWIS, G. E. USHER, and E. S. WAIGHT.

MESITYL OXIDE undergoes an exothermic reaction in the presence of lithium, to give a complex mixture from which the solid dimer (I) is readily isolated.[1] We now report on the nature of the liquid products.

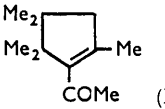
One component ($C_{12}H_{20}O$) is readily separable by distillation. Its infrared spectrum is very similar to that reported by Nahum [2] for the cyclic vinyl ether (II) obtained in the reduction of mesityl oxide with sodium amalgam. The nuclear magnetic resonance spectrum is consistent with this structure. An ether of this structure has also been obtained by the action of magnesium and acetic acid on mesityl oxide,[3] and we have shown that its infrared and nuclear magnetic resonance spectra are identical with those of the ether from the lithium reaction.



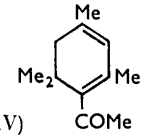
(I)



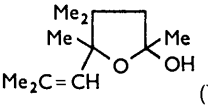
(II)



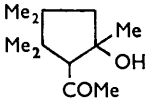
(III)



(IV)



(V)



(VI)

A second pure component can be obtained through its semicarbazone. Its infrared spectrum is almost identical with that of 2-acetyl-1,3,3,4,4-pentamethylcyclopentene (III) reported by Nahum,[2] and this structure is supported by the nuclear magnetic resonance spectrum. This ketone is also formed in the reduction with magnesium and acetic acid.

The high-boiling residue left on removal of these three compounds contains a conjugated dienone which has not been obtained pure. From the melting point and ultraviolet light absorption of its 2,4-dinitrophenylhydrazone it is probably the " isoxylitone " formulated as (IV) by Wiemann and his co-workers.[4]

The reaction of mesityl oxide with lithium thus gives products arising by base-catalysed dimerization, with and without dehydration, and by bimolecular reduction with dehydration. It is probable that compounds (II) and (III) are formed directly

[1] Braude, Gofton, Lowe, and Waight, *J.*, 1956, 4054.
[2] Nahum, *Ann. Chim.* (*France*), 1958, **3**, 108.
[3] Kolobielski, *Ann. Chim.* (*France*), 1955, **10**, 271.
[4] Wiemann, Sa-Le Thi-Thuan, and Conia, *Bull. Soc. chim. France*, 1957, 908; Wiemann, Furth, and Dana, *Compt. rend.*, 1960, **250**, 3674.

and not by dehydration of intermediates (V) and (VI), since significant amounts of these two alcohols cannot be detected, as they can be on bimolecular reduction with sodium amalgam or magnesium.

Experimental.—Microanalyses are by Miss J. Cuckney and the staff of the Organic Microanalytical Laboratory. Infrared spectra of liquid films were determined by Dr. R. L. Erskine and Mrs. A. I. Boston using a Grubb–Parsons S4 double-beam spectrometer. Nuclear magnetic resonance spectra of solutions in carbon tetrachloride were measured by Drs. L. M. Jackman and J. W. Lown using a Varian 4300 spectrometer, and are expressed as τ-values.[5]

Reaction of mesityl oxide and lithium. Procedure (*b*) described by Braude *et al.*[1] was used. The product (165 g.), b. p. 48—103°/3·5 mm. (from mesityl oxide, 250 g.), was freed from solid dimer (32 g.) and redistilled through a 2 ft. Stedman column.

2,3-*Dihydro*-2,3,3,5-*tetramethyl*-2-2′-*methylpropenylfuran* (II). This was the major (>95%) component of the fraction (9 g.) of b. p. 47°/0·9 mm., n_D^{26} 1·4570 (Found: C, 79·9; H, 11·1. Calc. for $C_{12}H_{20}O$: C, 79·9; H, 11·2%), $\nu_{max.}$ 3065w (=C–H), 1670s (C=C–O), 1067s, 1055s, 960s, 738s cm.$^{-1}$. Nuclear magnetic resonance (of italicized protons): 9·11, 9·00 [$\rangle C(CH_3)_2$]; 9·03 (trace, impurity); 8·80 [$\rangle C(CH_3)\cdot O\cdot$]; 8·32, 8·29, 8·27 [$C(CH_3)_2$=CH]; 8·20, 8·17 [$O\cdot C(CH_3)$=CH]; 5·71 (CH=C–O); 4·91 (CH=C$\langle$) p.p.m. Gas–liquid chromatography indicated the presence of a trace of a less volatile impurity which could not be removed by distillation or chromatography.

2-*Acetyl*-1,3,3,4,4-*pentamethylcyclopentene* (III). The fraction, b. p. 62—78°/4 mm. (53 g.), was treated with aqueous semicarbazide acetate. The bulk failed to react and was recovered (41 g.); it had b. p. 100—165°/2 mm., n_D^{26} 1·503—1·509. The semicarbazone, m. p. 170—171° (from ethanol) (Kolobielski [3] gives m. p. 166—166·5°), was hydrolysed by hot 0·5N-sulphuric acid, and the ketone extracted with ether. It had b. p. 70°/1 mm., n_D^{23} 1·4743, $\lambda_{max.}$ 252 mμ (ε 7900 in EtOH), $\nu_{max.}$ 1667vs (C=O), 1619m (C=C) cm.$^{-1}$. Nuclear magnetic resonance (for italicized protons): 9·12 [$\rangle C(CH_3)_2$]; 9·04 [$\rangle C(CH_3)_2$]; 8·11, 8·08, 8·05 [$-C(CH_3)$=C$\langle$]; *ca.* 7·85 ($\rangle CH_2$); 7·80 [$C(CH_3)$=O] p.p.m. The ketone gave a red 2,4-dinitrophenylhydrazone, m. p. 125·5—126·5° (from methanol) (Found: C, 59·9; H, 6·7; N, 15·6. Calc. for $C_{18}H_{24}N_4O_4$: C, 60·0; H, 6·7; N, 15·5%).

"*Isoxylitone.*" The residue, b. p. >103°/3·5 mm., was freed from further amounts of solid dimer and after redistillation had $\lambda_{max.}$ 237, 296 mμ ($E_{1\,cm.}^{1\%}$ 129, 270). It afforded a dark red 2,4-dinitrophenylhydrazone, which after chromatography on bentonite–kieselguhr and crystallization from methanol had m. p. 159—160° (Found: N, 15·7. Calc. for $C_{18}H_{22}N_4O_4$: N, 15·6%), $\lambda_{max.}$ 408 mμ (ε 22,600 in chloroform). Wiemann *et al.*[4] give for 1-acetyl-2,4,6,6-tetramethylcyclohexa-1,3-diene $\lambda_{max.}$ 235, 291 mμ (ε 4000, 13,000) and for its 2,4-dinitrophenylhydrazone m. p. 156°, $\lambda_{max.}$ 406 mμ (ε 24,000).

Bimolecular reduction of mesityl oxide.[3] To a stirred mixture of mesityl oxide (25 g.), acetone (63 ml.), water (28 ml.), and magnesium (10 g.) at −25° to −30° 90% aqueous acetic acid (60 ml.) was added in 4 hr. After the addition of further magnesium (10 g.) the mixture was kept below −20° for 18 hr. Unchanged magnesium was removed, the filtrate neutralized with saturated aqueous sodium carbonate, and acetone removed under a vacuum. The residue formed two layers; the aqueous layer was extracted with ether, and the ether extracts were combined with the organic layer, dried (Na_2SO_4), and distilled. This procedure was repeated four times, and the combined products (64 g., after separation of unchanged mesityl oxide) were redistilled through a 4 in. Stedman column. The fraction, b. p. 44°/0·8 mm., n_D^{22} 1·4601 (9 g.), had infrared and nuclear magnetic resonance spectra almost identical with the spectra of the ether reported above. Gas–liquid chromatography showed the presence of *ca.* 5% of a less volatile impurity. The residue, b. p. >60°/0·5 mm., $n_D^{25\cdot5}$ 1·4693, was treated with 2,4-dinitrophenylhydrazine sulphate in methanol. One of the products was soluble in boiling methanol; it had m. p. 125—126°, undepressed on admixture with the derivative of the ketone (III) obtained above. Kolobielski [3] reports no red 2,4-dinitrophenylhydrazone of this m. p. and gives 109—110° for the m. p. of the derivative of 2-acetyl-1,3,3,4,4-pentamethylcyclopentene.

We are indebted to Dr. L. M. Jackman for assistance in the interpretation of the nuclear magnetic resonance data.

Department of Chemistry, Imperial College of Science and Technology,
S. Kensington, London, S.W.7. [*Received, December 1st*, 1960.]

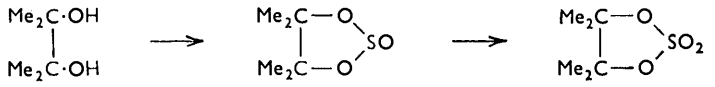
[5] Tiers, *J. Phys. Chem.*, 1958, **62**, 1151.

436. *Tetramethylethylene Sulphate.*

By Wilson Baker and B. F. Burrows.

Cyclic alkylene sulphates have been prepared by four general methods: (*a*) from 1,2- and 1,3-alkylene dibromides and silver sulphate;[1] (*b*) from 1,2- and 1,3-alkanediols with fuming sulphuric acid in chloroform;[2] (*c*) from cyclic sulphites by oxidation with calcium permanganate in acetic acid;[3] and (*d*) from 1,2- and 1,3-diacetoxyalkanes by distillation with dialkyl sulphates.[4] In a few cases other methods have been employed.[2,5]

Ethylene sulphate, previously made by methods (*a*) (22%) and (*d*) (66%), has now also been prepared by method (*c*) in 1% yield. Trimethylene sulphate, previously made by methods (*a*) (29%), (*b*) (10%), and (*d*) (70%), has now similarly been prepared by method (*c*) in 20% yield. Details of these experiments are not recorded because method (*d*) involving transalkylation (published after our work was completed in 1957) is certainly the best for preparing these cyclic sulphates. Tetramethylethylene sulphate (III), which was required for the preparation of highly *C*-methylated compounds, has now been prepared by method (*c*) from pinacol (I) by oxidation of the derived cyclic sulphite (II).[6] Other methods of preparation are complicated by the ease with which pinacol and its derivatives pass into pinacolone or into 2,3-dimethylbuta-1,3-diene.



(I) (II) (III)

Tetramethylethylene sulphate could not be prepared by treating pinacol with sulphuryl chloride in pyridine.

Experimental.—Tetramethylethylene sulphite (II). Anhydrous pinacol is not readily prepared from the hexahydrate by distillation with benzene as recommended in *Organic Syntheses*;[7] large volumes of benzene are required and pinacol is volatile in benzene vapour (pinacol hydrate crystallises from the distillate). Crude pinacol hexahydrate (20 g.) gave anhydrous pinacol, b. p. 168—174°, by the following methods: (*a*) dissolving it in acetone (100 ml.), shaking the solution with anhydrous sodium sulphate (50 g.), and recovery (yield 9·3 g.); (*b*) shaking it with light petroleum (b. p. 60—80°; 40 ml.) and anhydrous potassium carbonate (20 g.) at 40—45° for 10 min. and recovery (yield 7·3 g.); (*c*) distillation at ordinary pressure [yield 6·9 g.; pinacol hydrate (2 g.) was recovered from the filtrate]. The anhydrous pinacol (0·1 mole) was converted into tetramethylethylene sulphite (II) (34% yield) by treatment with purified thionyl chloride (0·2 mole) under the conditions given by Szmant and Emerson;[6] these authors claim a 55% yield but fail to record the relative amounts of the two reactants.

Tetramethylethylene sulphate (III). To tetramethylethylene sulphite (19·6 g.) in acetic acid (60 ml.) was added dropwise with stirring a solution of calcium permanganate (25·5 g.) in water (60 ml.), the temperature being kept below 15°, until, after the first rapid exothermic reaction, an excess of permanganate was present. Sulphur dioxide was now passed in at room temperature to remove manganese dioxide, and after dilution with an equal volume of water, the mixture was extracted three times with ethyl acetate (150, 100, and 50 ml.), and the combined

[1] Baker and Field, *J.*, 1932, 86.
[2] Lichtenberger and Lichtenberger, *Bull. Soc. chim. France*, 1948, **15**, 1002.
[3] Lichtenberger and Hincky, *Bull. Soc. chim. France*, 1951, **18**, 796; Garner and Lucas, *J. Amer. Chem. Soc.*, 1950, **72**, 5499; Brimacombe, Foster, Hancock, Overend, and Stacey, *J.*, 1960, 201.
[4] VEB Filmfabrik Agfa Wolfen, F.P. 1,171,347/1959.
[5] Methylene sulphate, Delépine, *Compt. rend.*, 1899, **129**, 831; *Bull. Soc. chim. France*, 1899, **21**, 1055; Baker, *J.*, 1931, 1765. Glyoxal sulphate, Ott, D.R.-P. 362,743; Ruggli and Henzi, *Helv. Chim. Acta*, 1929, **12**, 364; Baker and Field, *J.*, 1932, 86. See also Lichtenberger and Dürr, *Bull. Soc. chim. France*, 1956, 664. Cyclic sulphates of carbohydrates, prepared by reaction with sulphuryl chloride, Helferich *et al.*, *Ber.*, 1921, **54**, 1082; 1923, **46**, 1083; 1925, **58**, 886; Jones *et al.*, *Canad. J. Chem.*, 1959, **37**, 1412; 1960, **38**, 1122.
[6] Szmant and Emerson, *J. Amer. Chem. Soc.*, 1956, **78**, 454.
[7] *Org. Synth.*, 1942, **22**, 40.

extracts were shaken with water, then with an excess of aqueous sodium hydrogen carbonate, dried ($CaCl_2$), and distilled under reduced pressure. The remaining product solidified and was crystallised from benzene–light petroleum (b. p. 60—80°) giving *tetramethylethylene sulphate* as needles (yield 11·2 g.), decomp. 131° [Found: C, 39·8; H, 6·7; S (as sulphate by hydrolysis), 17·4. $C_6H_{12}O_4S$ requires C, 40·0; H, 6·7; S, 17·7%].

We thank the Department of Scientific and Industrial Research for a Studentship awarded to B. F. B.

THE UNIVERSITY, BRISTOL. [*Received, December 5th*, 1960.]

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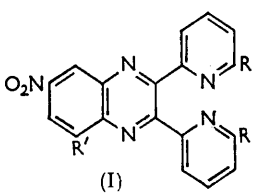
437. *Carcinogenic Nitrogen Compounds. Part XXX.*[1] *2,3-Dipyridylquinoxalines and 5,6-Dipyridylpyrido(2′,3′-2,3)pyrazines.*

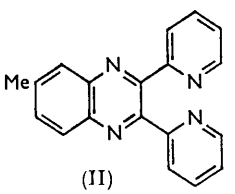
By NG. PH. BUU-HOÏ and G. SAINT-RUF.

CARCINOGENIC substances have often been encountered among heterocyclic molecules containing several nuclear nitrogen atoms, *e.g.*, dinaphthopyrazines,[2] which produce bladder tumours and sarcomas, and tricycloquinazoline, which is carcinogenic in mice both on injection and on skin-painting.[3] The present Note reports the synthesis of some polycyclic compounds bearing the pyrazine nucleus and pyridyl substituents, prepared for biological testing.

Condensation of 4-nitro-1,2-phenylenediamine with 2,2′-pyridil and 6,6′-dimethyl-2,2′-pyridil in ethanol yielded 6-nitro-2,3-di-(2-pyridyl)- (I; R = R′ = H) and 6-nitro-2,3-di-(6-methyl-2-pyridyl)-quinoxaline (I; R = Me, R′ = H) respectively. Similar condensations of 2,2′-pyridil with 4-methyl- and 3-chloro-5-nitro-1,2-phenylenediamine afforded 6-methyl-2,3-di-(2-pyridyl)- (II) and 5-chloro-7-nitro-2,3-di-(2-pyridyl)-quinoxaline (I; R = Me, R′ = Cl); 1,2-naphthylenediamine and 2,2′-pyridil gave 2,3-di-(2-pyridyl)-5,6-benzoquinoxaline (III). Whilst the above condensations all took place in a matter of minutes, 2,3-diaminopyridine reacted sluggishly, and 5,6-di-(2-pyridyl)- (IV; R = H) and 5,6-di-(6-methyl-2-pyridyl)-pyrido(2′,3′-2,3)pyrazine (IV; R = Me) were obtained only after several hours' heating.



(I)



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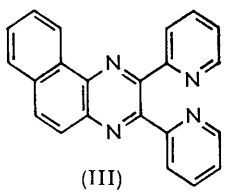
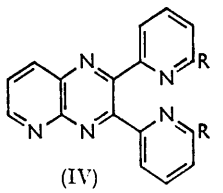


(III)



(IV)

In preliminary tests in rats, the compounds of type (I) showed considerable toxicity towards the liver when given by injection.

[1] Part XXIX, Marty, Buu-Hoï, and Jacquignon, *J.*, 1961, 384.
[2] Rudali, Chalvet, and Winternitz, *Compt. rend.*, 1955, **240**, 1738; Hackmann, *Z. Krebsforschung*, 1951, **58**, 56.
[3] Baldwin, Butler, Cooper, and Partridge, *Nature*, 1958, **181**, 838; Baldwin, Cunningham, and Partridge, *Brit. J. Cancer*, 1959, **13**, 94.

Experimental.—6-*Nitro*-2,3-*di*-(2-*pyridyl*)*quinoxaline*. A solution of 2,2′-pyridil (10 g.) and 4-nitro-1,2-phenylenediamine (7 g.) in ethanol (150 c.c.) was refluxed for 45 min. The orange solid formed on concentration of the solution and cooling was collected and recrystallised from ethanol in presence of charcoal to remove the red impurity, giving the *quinoxaline* as yellowish prisms (12 g.), m. p. 193° (Found: N, 21·0. $C_{18}H_{11}N_5O_2$ requires N, 21·3%).

6-*Nitro*-2,3-*di*-(6-*methyl*-2-*pyridyl*)*quinoxaline*, similarly obtained from 6,6′-dimethyl-2,2′-pyridil (10 g.) and 4-nitro-1,2-phenylenediamine (6·3 g.) in ethanol (150 c.c.), formed pale yellow needles (13 g.), m. p. 191°, from ethanol–benzene (Found: C, 66·9; H, 4·5; N, 19·4. $C_{20}H_{15}N_5O_2$ requires C, 67·2; H, 4·2; N, 19·6%).

6-*Methyl*-2,3-*di*-(2-*pyridyl*)*quinoxaline*, prepared from 2,2′-pyridil (6 g.) and 4-methyl-1,2-phenylenediamine (3·5 g.) in ethanol (100 c.c.), crystallised as colourless prisms (7·5 g.), m. p. 142°, from cyclohexane (Found: C, 76·4; H, 5·0; N, 18·6. $C_{19}H_{14}N_4$ requires C, 76·5; H, 4·7; N, 18·8%).

5-*Chloro*-7-*nitro*-2,3-*di*-(2-*pyridyl*)*quinoxaline*, obtained from 2,2′-pyridil (10 g.) and 3-chloro-5-nitro-1,2-phenylenediamine (9 g.) in ethanol (150 c.c.), formed yellow needles (15 g.), m. p. 194°, from ethanol (Found: N, 19·0. $C_{18}H_{10}ClN_5O_2$ requires N, 19·2%).

2,3-*Di*-(2-*pyridyl*)-5,6-*benzoquinoxaline*. A solution of 2,2′-pyridil (2 g.) and 1,2-naphthylenediamine (1·5 g.) in ethanol (50 c.c.) was refluxed for 3 hr., the solvent distilled, and the residue crystallised from cyclohexane, giving colourless prisms (2 g.), m. p. 146° (Found: C, 79·0; H, 4·2; N, 16·6. $C_{22}H_{14}N_4$ requires C, 79·0; H, 4·2; N, 16·7%).

5,6-*Di*-(2-*pyridyl*)*pyrido*(2′,3′-2,3)*pyrazine*. 2,3-Diaminopyridine (m. p. 112°) was prepared from 2-amino-3-nitropyridine by Tschitschibabin and Kirssanow's method; [4] a solution of this diamine (3 g.) and 2,2′-pyridil (5·8 g.) in ethanol (50 c.c.) was refluxed for 18 hr., and the solvent was distilled off; the residue recrystallised from heptane as colourless needles (5 g.), m. p. 146° (Found: C, 71·4; H, 4·2; N, 24·3. $C_{22}H_{11}N_5$ requires C, 71·6; H, 3·9; N, 24·6%). When the heating was reduced to 45 min., no condensation product could be isolated and the reagents were mostly recovered.

5,6-*Di*-(6-*methyl*-2-*pyridyl*)*pyrido*(2′,3′-2,3)*pyrazine*, similarly obtained from 2,3-diaminopyridine (1·5 g.) and 6,6′-dimethyl-2,2′-pyridil (3·3 g.) in ethanol (25 c.c.), formed colourless prisms (3 g.), m. p. 155°, from heptane (Found: C, 72·5; H, 5·0; N, 22·2. $C_{19}H_{15}N_5$ requires C, 72·7; H, 4·8; N, 22·4%).

This investigation was supported in part by a research grant from the National Cancer Institute of the National Institutes of Health, U.S. Public Health Service; the authors thank the authorities concerned.

THE RADIUM INSTITUTE, THE UNIVERSITY OF PARIS. [*Received, December 7th*, 1960.]

[4] Tschitschibabin and Kirssanow, *Ber.*, 1927, **60**, 766.

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438. *Bis(triphenylphosphine)nickel Dinitrosyl.*

By W. P. GRIFFITH, J. LEWIS, and G. WILKINSON.

BIS(TRIPHENYLPHOSPHINE)NICKEL DICARBONYL has been found to react with nitric oxide in benzene solution, to give a dark purple crystalline complex $[(C_6H_5)_3P]_2Ni(NO)_2$. The compound has been shown to be diamagnetic, monomeric in benzene, and a non-electrolyte in nitrobenzene. In the infrared spectrum there is only one sharp N–O stretching frequency, at 1745 cm.$^{-1}$, in the region characteristic for NO^+ co-ordination complexes.[1,2] Isotopic substitution, by use of ^{15}NO, has shown this frequency to move to 1706 cm.$^{-1}$, which agrees very well with the calculated ($\sqrt{30/31}$) displacement to 1705 cm.$^{-1}$. Since only one frequency is observed, and it has not been possible to resolve this band, even on a grating instrument, for chloroform and carbon tetrachloride solutions, the possibility of two equivalent co-ordinated NO^+ groups in a tetrahedral or a *cis*-planar structure can be excluded. If the molecule is tetrahedral, the observations are consistent only with the

[1] Lewis, Irving, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 32.
[2] Griffith, Lewis, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 38.

requirement that the other NO group is present as a co-ordinated NO^- group. However, no absorption in the region characteristic of NO^- groups [2] was observed owing to intense absorption by the triphenylphosphine ligand in this region. A possible formulation as a planar *trans*-structure was excluded as the complex was found to have a dipole moment of 4·26 D (at 30°) in benzene, which may be compared with the dipole moment [3] of the tetrahedral bis(triphenylphosphine)nickel dicarbonyl of 3·82 D. From *X*-ray powder patterns, we have shown, however, that the dicarbonyl and the nitrosyl compounds are not isomorphous. On the present formulation for the dinitrosyl the nickel is formally in the zero oxidation state with a tetrahedral stereochemistry for the molecule.

This nickel nitrosyl compound can thus be considered as the parent of the triphenylphosphinenickel nitrosyl bromide, $[(C_6H_5)_3P]_2NiNOBr$,[4] where the N–O stretching frequency occurs at 1735 $cm.^{-1}$, in which the NO^- is replaced by Br^-.

We also prepared the corresponding triphenyl phosphite dinitrosyl complex where the N–O stretching frequency appears at 1710 $cm.^{-1}$; similar products were obtained by the action of nitric oxide on tributyl- and tripropyl-phosphinenickel dicarbonyls, but the purple products were oils and could not be obtained analytically pure.

The situation in which an identical ligand molecule, *i.e.*, NO, can be bound simultaneously to an atom in a radically different way is somewhat unusual, and it might have been expected that by some electronic mechanism the two groups would have been made equivalent. It has been recently suggested,[5] on the basis of ultraviolet absorption spectra, that in the red nitrosopentamminecobalt derivatives, where the nitric oxide was considered to be bound as NO^- from the infrared criterion,[2] that the nitric oxide may be bound through the oxygen atom, *i.e.*, as Co–O–N. The inequivalence of the two NO groups in the dinitrosyl nickel derivatives can thus be readily understood, although there is at the present time no unequivocal evidence to favour bonding through oxygen.

Experimental.—Microanalyses and molecular-weight determinations (ebullioscopic in benzene) were made by the Microanalytical Laboratory of this College.

Preparations. Bis(triphenylphosphine)nickel dicarbonyl (4 g.) in anhydrous benzene (80 ml.) was treated with nitric oxide for 3 hr. The purple product, *bis(triphenylphosphine)-nickel dinitrosyl*, was recrystallised from light petroleum (b. p. 40—60°)–benzene and dried *in vacuo* (yield, 3 g., 70%) (Found: C, 66·7; H, 4·5; N, 4·3; P, 9·2; Ni, 8·9%; *M*, 648. $C_{36}H_{30}N_2NiO_2P_2$ requires C, 67·2; H, 4·7; N, 4·4; P, 9·7; Ni, 9·1%; *M*, 642). The complex is stable in air and is unaffected by dilute acids. It is readily soluble in benzene, chloroform, alcohol, and similar solvents, the solutions slowly decomposing in air, especially those in chlorinated solvents.

In a similar manner, *bis(triphenyl phosphite)nickel dinitrosyl* (Found: C, 57·9; H, 4·6; N, 3·8; Ni, 8·2. $C_{36}H_{30}N_2NiO_8P_2$ requires C, 58·8; H, 4·1; N, 3·8; Ni, 8·0%) was prepared.

The isotopically substituted triphenylphosphine compound was prepared by using ^{15}NO (66%) prepared from the reaction of potassium nitrite with sulphuric acid and potassium iodide.

Physical measurements. Infrared spectra were measured on Perkin–Elmer model 21 and Grubb–Parsons grating instruments for Nujol mulls and for carbon tetrachloride and chloroform solutions.

The dipole moment was measured for benzene solution (seven concentrations) by means of a standard heterodyne-beat-type instrument with a modified Sayce–Briscoe cell, and the procedure described previously.[6]

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[3] Chatt and Hart, *J.*, 1960, 1378.
[4] Feltham, *J. Inorg. Nuclear Chem.*, 1960, **14**, 307.
[5] Yamada, Nishikawa, and Tsuchida, *Bull. Chem. Soc. Japan*, 1960, **33**, 930.
[6] Burton, Pratt, and Wilkinson, *J.*, 1960, 4290.