

NOTES.

576. *Tracer Studies in Ester Hydrolysis. Part XIII.¹ Cyclic and Dialkyl Selenites.*

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DIALKYL selenites have been prepared from the alkyl halide and silver selenite, and from the sodium alkoxide and selenyl chloride,² and also by direct reaction between selenium dioxide and the alcohol.³ Selenite esters are postulated intermediates in the oxidation of ketones by selenium dioxide,⁴ and spectroscopic studies of selenious acid and selenium dioxide in methanol or ethanol show that the esters are present in these mixtures.⁵

¹ Part XII, Bunton and Hendy, preceding paper.

² Strecker and Daniel, *Annalen*, 1928, **462**, 186.

³ Mel'nikov and Rokitskaya, *J. Gen. Chem. (U.S.S.R.)*, 1937, **7**, 1543; *Chem. Abs.*, 1937, **31**, 8502; Simon and Heintz, *Naturwiss.*, 1960, **47**, 468.

⁴ Waitkins and Clark, *Chem. Rev.*, 1945, **36**, 235; Corey and Schaefer, *J. Amer. Chem. Soc.*, 1960, **82**, 918; Schaefer, *ibid.*, 1962, **84**, 713, 717.

⁵ Paetzold and Simon, *Z. anorg. Chem.*, 1960, **303**, 53; Paetzold and Rönsch, *ibid.*, 1962, **314**, 91.

The present work shows that selenite esters behave similarly to sulphite esters.⁶ They are hydrolysed with complete selenium–oxygen fission (Table 1), and the heats of saponification of the cyclic and open-chain esters are very similar. However, they are much more

TABLE 1.
Bond fission.

Selenite Reagent	Diethyl			Di-isopropyl	
	2M-NaOH	—	M-HClO ₄	2M-NaOH	M-HClO ₄
$N_{\text{ROH}} \dots\dots\dots$	0.01 ₆	0.01 ₄	0.00 ₈	0.01 ₆	0.00 ₄
$[\text{Me}\cdot\text{CHO}]/[\text{EtOH}] \dots\dots\dots$	2	3	4	—	—

Isotopic abundance, N , in atom % excess. $N_{\text{H}_2\text{O}}$ 0.87 atom % excess; diluted by addition of solid NaOH, or 72% HClO₄. The amount of NaOH was slightly greater than that required for complete saponification.

reactive than the corresponding sulphites and, although hydrolysed readily in acid and rapidly in alkali, sulphites are unreactive to water. We were unable to measure the rate of hydrolysis of the selenite esters either by conductivity or by titration. Titration with aqueous sodium hydroxide gave complete hydrolysis even when a selenite ester was first dissolved in acetone at -80° ; and when the selenite was added to conductivity water at 0° the conductivity was approximately that of the equivalent solution of selenious acid. The thermochemical results show that the hydrolysis is very fast, because the rise of temperature during saponification of diethyl and ethylene selenite was as rapid as for the neutralisation of selenious acid. These observations, and the ease of reaction between selenious acid and selenium dioxide and the alcohols, show that nucleophilic attack upon the selenium atom of a selenite is much faster than upon the sulphur atom of a sulphite. The failures to resolve selenoxides, although optically active sulphoxides are known, has been ascribed to hydration of the selenoxide.⁷ Dialkyl selenites are hydrolysed much more rapidly than dimethyl selenate,¹ in accord with the general rule that for a given heteroatom nucleophilic attack upon this atom will be fastest for the ester of the least oxygenated, weaker, acid.

TABLE 2.

Reactant or solute	Heats of reaction and solution.				
	(EtO) ₂ SeO	(-CH ₂ -O) ₂ SeO	EtOH	(CH ₂ -OH) ₂	H ₂ SeO ₃
Reaction	Sapon.	Sapon.	—	—	Neut.
$-\Delta H$ (kcal. mole ⁻¹)	33	28.5	3.3	1.5	22.5

For duplicate saponifications ΔH agreed within 0.5 kcal. mole⁻¹. The heat of solution of dioxan (5 c.c.; $-\Delta H = 0.13$ kcal.) has been deducted.

Five-membered cyclic phosphates⁸ and sulphates⁹ are much more reactive than the open-chain esters, and part of the effect is caused by different stabilities of the initial states, because heats of hydrolysis of the reactive five-membered cyclic esters are greater than those of the less reactive esters. It is suggested that the partial double-bonding between the oxygen atoms of the ring and the heteroatom, which should stabilise the initial state, should be less pronounced in the five-membered cyclic phosphates and sulphates than in the open-chain esters.⁸⁻¹⁰ This double-bonding should be less important in the esters of lower oxidation states which have unshared pairs of electrons on the heteroatom, and the heats of hydrolysis of five-membered cyclic sulphites are "normal." Our work shows that this is true also for the selenites, and therefore these differences in

⁶ Bunton, de la Mare, and Tillett, *J.*, 1959, 1766; Tillett, *J.*, 1960, 37; de la Mare, Tillett, and van Woerden, *Chem. and Ind.*, 1961, 1533.

⁷ Campbell, Walker, and Coppinger, *Chem. Rev.*, 1952, 50, 279.

⁸ Kumamoto, Cox, and Westheimer, *J. Amer. Chem. Soc.*, 1956, 78, 4858; Haake and Westheimer, *ibid.*, 1961, 83, 1102.

⁹ Kaiser, Panar, and Westheimer, *J. Amer. Chem. Soc.*, in the press.

¹⁰ (a) Pagdin, Pine, Tillett, and van Woerden, *J.*, 1962, 3835; (b) Davis, *J. Amer. Chem. Soc.*, 1962, 84, 599.

heats of reaction appear to depend on the oxidation state of the heteroatom rather than upon its size. The total heat of reaction is very close to the heats of solution and neutralisation of the products (Table 2). We plan to test these hypotheses about the stabilities of the initial states of these esters by studying the selenates.

Cyclic carbonates are more reactive to nucleophiles than dialkyl carbonates,¹¹ but their behaviour is similar to that of the lactones rather than the cyclic esters of inorganic esters, because $\alpha\gamma$ -cyclic carbonates are more reactive than their $\alpha\beta$ -isomers; it would be interesting to know whether the heats of saponification differ.

A small amount of acetaldehyde was formed during the hydrolysis of diethyl selenite, and some selenium was deposited: added acid increased the amount of oxidation (Table 1). Mixtures of selenious acid and aqueous ethanol did not form acetaldehyde, which therefore arose from a reaction involving either diethyl or ethyl hydrogen selenite. No acetone was isolated on hydrolysis of di-isopropyl selenite.

Experimental.—The esters were prepared by heating dry selenium dioxide (25 g.) in the alcohol (50 c.c.), under reflux (for the diethyl and the di-isopropyl ester) or at 100° (for ethylene selenite), until most of the selenium dioxide had dissolved ($\frac{1}{2}$ —2 hr.). The solution was filtered if necessary, then concentrated by distillation (*in vacuo* for ethylene selenite), and more alcohol was added. The solution was concentrated again and the ester was obtained from the residue by vacuum-distillation (for the diethyl and di-isopropyl selenite) or by crystallisation. Our materials had the following properties:

Diethyl selenite, after redistillation *in vacuo*, b. p. 58°/4 mm., n^{20} 1.4662, n^{25} 1.4548 (lit.,² n^{23} 1.4625—1.4788) (Found: Se, 40.6. Calc. for $C_4H_{10}O_3Se$: Se, 40.5%).

Di-isopropyl selenite, after redistillation *in vacuo*, b. p. 50°/1.5 mm. [Found: C, 34.0; H, 6.4; Se, 36.7%; M (sapon.), 212. $C_6H_{14}O_3Se$ requires C, 33.8; H, 6.6; Se, 37.0%; M , 213].

Ethylene selenite, after recrystallation in benzene, m. p. 62—66° [Found: C, 15.5; H, 2.7; Se, 51.0%; M (sapon.), 161, (Rast) 156. Calc. for $C_2H_4O_3Se$: C, 15.5; H, 2.6; Se, 50.8%; M , 155]. This ester was also prepared by heating selenium dioxide in refluxing ethylene glycol for 1 hr. The water and excess of glycol were removed by leaving the liquid for several months in a vacuum-desiccator containing calcium chloride.

We did not obtain an ester from reaction between selenium dioxide and t-butyl alcohol.

The esters were colourless, but decomposed to give selenium at 80—100°. They rapidly absorbed water from the atmosphere and were handled in a dry-box. Their infrared spectra showed no absorption due to hydroxyl groups.

Diethyl selenite (liquid) had strong infrared bands at 7.2, 9.1, 9.9br, 10.6, and 11.4, and a very broad band at 15.5—17 μ ; there were weak bands at 6.1, 7.3, 7.8, 8.7, and 12.3 μ and a shoulder at 9.6 μ .

Di-isopropyl selenite (liquid) had strong bands at 6.8, 7.3(d), 8.8, 9.1, 11.0, 12.1, and 15.5 μ , a shoulder at 10.6 μ , and medium bands at 7.4 and 8.5 μ . Ethylene selenite (in Nujol) had strong bands at 9.9, 11.3br, and 15.5—17 μ , a medium doublet at 10.9—11 μ , and weak bands at 8.2, 8.3, 9.0, and 10.3 μ . The spectra of these dialkyl selenites are similar to those of other dialkyl selenites.⁵ The selenium content of the esters was determined iodometrically.

Hydrolysis. Solutions of these esters in water, or in dry acetone at -80° , could be titrated with sodium hydroxide to a first neutralisation point which corresponded to that calculated, by using Bromothymol Blue as indicator. The second neutralisation point could just be observed by using Alizarin Yellow as indicator.

Addition of diethyl or ethylene selenite to conductivity water at 0° immediately gave a conductivity which was similar to that of an equivalent solution of selenious acid. Bright platinum electrodes were used to avoid catalysis. The equivalent conductance of 0.1—0.001M-solutions of selenious acid at 0° fitted the Oswald dilution law, with $\Lambda_0 = 260 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$, and $10^3K = 3.1 \text{ mole l.}^{-1}$ (lit.,¹² $10^3K = 4.0 \text{ mole l.}^{-1}$ at room temperature).

Solutions of the esters had equivalent conductances ($\text{ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$) at 0° as follows: $2.43 \times 10^{-3}M\text{-Et}_2\text{SeO}_3$ had $\Lambda = 158$ (168); $8.51 \times 10^{-3}M\text{-ethylene selenite}$ had $\Lambda = 118$ (116); $8.51 \times 10^{-4}M\text{-ethylene selenite}$ had $\Lambda = 218$ (206). The values in parentheses are for equivalent solutions of H_2SeO_3 .

¹¹ Pohoryles, Levin, and Sarel, *J.*, 1960, 3082 and refs. therein.

¹² Wilcox and Prideaux, *J.*, 1925, 127, 1543.

Bond fission. The ester (*ca.* 3 g.) was added to stirred H_2^{18}O (*ca.* 25 c.c.) at 25° . Selenium was deposited during hydrolysis of diethyl selenite, the heaviest deposit being from the acid hydrolysis which also gave most acetaldehyde. After 30 min. the solution was neutralised, and a water-alcohol mixture pumped off. The alcohol was concentrated by distillation through a low-hold-up spiral-packed column (250×6 mm.), and was purified by gas-liquid chromatography through a 6 ft. glycerol-Celite column. A peak corresponding to acetaldehyde was found for the samples isolated after hydrolysis of diethyl selenite. The purified alcohols were pyrolysed *in vacuo* in a red-hot carbon tube in a radio-frequency induction furnace, and the carbon monoxide was analysed mass-spectrometrically.

Heat of reaction. The procedure of Pagdin, Pine, Tillett, and van Woerden was followed.^{10a} The calorimeter was a Dewar flask (1 l.), and the stirrer was driven at 140 r.p.m. by a constant-speed motor. The calibration-heater and ampoule-breaker were those used by others; temperature changes were read on a Beckmann thermometer.

The ester (*ca.* 4 mmoles in dried dioxan, 5 c.c.) in a sealed ampoule was left overnight in 0.02N-sodium hydroxide (500 c.c.) in the calorimeter. The determination was made by breaking the ampoule and measuring the adiabatic change of temperature. The heat capacity of the apparatus was then measured electrically.

The heats of solution of ethanol and ethylene glycol, and the heat of neutralisation of selenious acid, were also measured. It is impossible to measure the heats of solution of the esters, but they are almost certainly small and similar (*cf.* ref. 10b).

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577. *Electron-spin Resonance Studies of Phosphonitrilic and Borazole Ring Systems.*

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CONSIDERABLE discussion has taken place on the extent of delocalisation in phosphonitrilic ring systems. Craig¹ has suggested that delocalised π -bonding analogous to that in benzene occurs, arising from overlap of the d_{xz} orbitals of phosphorus with the p_z orbital of nitrogen. Dewar *et al.*,² however, suggest a more restricted π -bonding system.

We have attempted to study the delocalisation in these systems, with the aid of electron-spin resonance spectroscopy, by treating phosphazenes with sodium, potassium, and sodium-potassium alloy in dimethoxyethane (to form the ions $\text{P}_3\text{N}_3\text{R}_6^-$ and $\text{P}_4\text{N}_4\text{R}'_8^-$), but no radicals are detected when $\text{R} = \text{NMe}_2$, NEt_2 , Me, or Cl, or when $\text{R}' = \text{NMe}_2$, NEt_2 , Me, F, or OEt.

Since it is relatively easy to prepare the radical-ions of benzene derivatives, we also carried out similar studies with $\text{P}_3\text{N}_3\text{Ph}_6$, considering that the unpaired electron may be delocalised over the aromatic and also the inorganic ring system. We realised that the hyperfine structure obtained from these negative ions would probably be complex but argue that the splitting due to the phosphorus and nitrogen atoms should be easily recognised. The reaction of these compounds with sodium or potassium, even at -78° , is rapid and certainly produces radicals; however, superimposed on the complex background of hyperfine lines is the spectrum which we recognise to be that of the biphenyl negative-ion.³ This radical-ion is stable at room temperature, unlike the radicals which produce the background structure. This shows that the phosphorus-phenyl bond has been severed, probably together with break-up of the phosphazene ring. We do not

¹ Craig, *J.*, 1959, 997.

² Dewar, Lucken, and Whitehead, *J.*, 1960, 2423.

³ Carrington and Dos Santos-Veiga, *Mol. Phys.*, 1962, 5, 21.

consider it worthwhile to attempt to analyse the spectra produced (at least twenty-five groups of lines are visible in the case of $P_3N_3Ph_6$ and any splitting arising from the phosphorus and nitrogen atoms is not easily discernible). Our attempts to obtain the spectrum of triphenylphosphine negative-ion in a similar manner also produced the biphenyl negative-ion.

The borazoles, $(RBNR')_3$ ($R = H, R' = Me$; $R = Me, R' = H$; $R = R' = Me$; $R = R' = Ph$; $R = Cl, R' = H$), do not give rise to electron-spin resonance spectra although, when R or R' (or both) = Me , the blue coloration attributed to the ether solutions of potassium or sodium-potassium alloy is much more intense than with ether alone.

Electrolysis of some of the compounds in acetonitrile with tetrapropylammonium perchlorate as a supporting electrolyte⁴ gave polarographic waves at a dropping-mercury electrode. However, electrolysis *in situ* in the electron-spin resonance cavity does not give any detectable resonances. Either, the radicals produced with phosphonitrilic or borazole ring systems are too short-lived to be observed, or the resonances are extremely broad (>100 gauss).

A Varian electron-spin resonance spectrometer was used in this work.

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⁴ Maki and Geske, *J. Chem. Phys.*, 1960, **33**, 825.

578. Arylhydroxylamines. Part III.¹ Reactions with Aldehydes.

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THE known condensation of arylhydroxylamines with aromatic aldehydes² to yield nitrones has now been observed in the reaction of phenylhydroxylamine and *N*-hydroxyanthranilic acid with pyridoxal 5'-phosphate. When solutions of nitrones are heated with potassium ferrocyanide, the colours produced are identical with those obtained from the parent hydroxylamines. With benzaldehydes, nitrones in acid solution undergo exchange of benzylidene radicals. 4-Dimethylaminocinnamaldehyde reacts with *N*-aryl-nitrones to yield coloured *N*-oxides, a reaction used for the detection of nitrones on paper chromatograms (see Experimental section). An alcoholic solution of 2-hydroxybenzylideneaniline *N*-oxide and *p*-nitrobenzaldehyde deposits 4-nitrobenzylideneaniline *N*-oxide quantitatively. Cysteine hydrochloride and *N*-acetylcysteine react with 4-chloro-, 2,4-dichloro-, 5-hydroxy-2-nitro-, and 2- and 4-nitro-benzylideneaniline *N*-oxide, and with the products from phenylhydroxylamine and pyridoxal 5'-phosphate or glucuronolactone, but not with 4-dimethylaminocinnamylideneaniline *N*-oxide; these reactions yield *S*-*p*-aminophenylcysteine and *S*-*p*-aminophenylmercapturic acid, respectively; the *S*-arylation of thiols has also been described for phenyl- and 2-naphthyl-hydroxylamines.³ The nitrone reaction is reversed in acid solution, carbonyl compounds being released;⁴ and triphenylnitronone in water yields *p*-aminophenol (presumably by rearrangement of phenylhydroxylamine) and benzophenone.⁵

The product from the reaction of phenylhydroxylamine with glucuronolactone is indistinguishable from the benzylideneaniline *N*-oxides in its reaction with benzaldehydes,

¹ Part II, Boyland and Nery, *J.*, 1962, 5217.

² Bellavita, *Gazzetta*, 1935, **65**, 755, 889.

³ Boyland, Manson, and Nery, *J.*, 1962, 606.

⁴ Krohnke, G.P. 736,978/1943, 755,943/1953; Smith, *Chem. Rev.*, 1938, **23**, 228.

⁵ Staudinger and Miescher, *Helv. Chim. Acta*, 1919, **2**, 334.

Aldehyde precursor Aniline N-oxides	Yield (%)	M. p. ¹	Solvent ²	Colour ³	Found (%)			Required (%)			$\nu(\text{N} \rightarrow \text{O})$ (cm.^{-1})	$\nu(\text{C}=\text{N})$ (cm.^{-1})		
					C	H	N	C	H	N				
Benzaldehyde ⁴	80	114 ⁵	c	—	—	—	—	—	—	—	—	1548	1595 ¹⁶ 1577 ¹⁶	
<i>p</i> -Chlorobenzaldehyde ⁵	82	152	c	—	—	—	—	—	—	—	—	—	—	
5-Hydroxy-2-nitrobenzaldehyde	84	220	a	Yellow	60.4	4.0	10.4	60.5	3.9	10.8	—	—	—	
2,3-Dihydroxybenzaldehyde	60	158	a	Yellow	67.9	4.7	6.2	68.1	4.8	6.1	—	—	—	
2,5-Dihydroxybenzaldehyde	50	174	b	Golden ¹⁷	67.8	4.8	6.3	—	—	—	—	—	—	
<i>p</i> -Dimethylaminobenzaldehyde ⁶	76	138	c	Yellow	—	—	—	—	—	—	—	—	—	
<i>p</i> -Dimethylaminocinnamaldehyde	78	203	c	Ochre ¹⁸	76.9	6.5	10.5	76.7	6.8	10.5	—	—	1534	1613
2,4-Dichlorobenzaldehyde ⁷	98	101	a	Buff	58.8	3.8	5.0	58.7	3.4	5.3	—	—	1538	1600
<i>o</i> -Carboxybenzaldehyde, +H ₂ O ⁸	85	116	c	—	64.7	5.2	5.6	64.9	5.1	5.4	—	—	1541	1582
Pyridoxal 5'-phosphate, +H ₂ O ⁹	65	168	b	Orange	47.0	4.8	—	47.2	4.7	—	—	—	—	—
3,4-Dimethylaniline N-oxides														
<i>o</i> -Nitrobenzaldehyde	96	132	d	Yellow	66.5	5.5	10.4	66.6	5.2	10.4	—	—	—	—
<i>p</i> -Nitrobenzaldehyde	96	163	d	Yellow	66.7	5.5	10.1	—	—	—	—	—	—	—
Salicylaldehyde	90	133	d	Yellow	75.2	6.6	5.6	74.7	6.3	5.8	—	—	—	—
<i>p</i> -Chlorobenzaldehyde ¹⁰	92	110	d	—	69.0	5.4	5.6	69.3	5.4	5.4	—	—	1555	1595
2,4-Dichloro-benzaldehyde ¹¹	92	132	d	Yellow ¹⁷	61.3	4.3	4.9	61.3	4.4	4.7	—	—	1541	1585
5-Hydroxy-1-nitrobenzaldehyde	88	232	d	Yellow	62.7	4.8	9.4	62.9	4.9	9.8	—	—	—	—
2,5-Dihydroxybenzaldehyde	75	142	d	Orange	69.6	6.2	5.4	70.0	5.9	5.4	—	—	—	—
2,4-Dihydroxybenzaldehyde	77	178	d	Yellow	70.4	6.3	5.5	—	—	—	—	—	—	—
<i>p</i> -Dimethylaminobenzaldehyde	75	144	d	Orange	75.8	7.2	10.7	76.1	7.5	10.4	—	—	—	—
4-Dimethylaminocinnamaldehyde	75	172	d	Reddish-brown	77.3	7.7	9.3	77.5	7.5	9.5	—	—	1538	1600
<i>o</i> -Carboxybenzaldehyde	96	150	d	Buff	71.2	5.8	5.0	71.4	5.6	5.2	—	—	—	—
2,4-Dinitrobenzaldehyde, + $\frac{1}{2}$ H ₂ O ¹²	96	175	d	Yellow ¹⁷	55.6	3.9	13.1	55.5	4.3	13.0	—	—	—	—
<i>o</i>-Carboxyaniline N-oxides														
<i>o</i> -Nitrobenzaldehyde	88	135	d	Orange	58.5	3.7	10.2	58.7	3.5	9.8	—	—	—	—
<i>p</i> -Nitrobenzaldehyde	90	152	d	Buff	58.8	3.6	10.1	—	—	—	—	—	—	—
2,4-Dichlorobenzaldehyde ¹³	95	168	d	—	54.3	2.9	4.6	54.2	2.9	4.5	—	—	—	—
Pyridoxal 5'-phosphate, ¹⁴ + $\frac{1}{2}$ H ₂ O	75	229	b	Yellow	46.0	4.2	6.6	46.0	4.1	7.1	—	—	—	—
Compound														
2,4-C ₈ H ₃ Cl ₂ -CH=N(O)-C ₁₀ H ₇ -2 ¹⁵	98	160	d	Yellow	64.7	3.2	4.2	64.6	3.5	4.4	—	—	1548	1585

¹ With decomp. ² (a) 50%, (b) 30%, and (c) 99.5% aqueous ethanol. ³ The nitrones are light-sensitive and become darker in daylight. They form needles, except as otherwise noted. ⁴ Wheeler and Gore (*J. Amer. Chem. Soc.*, 1956, **78**, 3363) record m. p. 114°. ⁵ Bellavita (ref. 2) records m. p. 153°. ⁶ Splitter and Calvin (*J. Org. Chem.*, 1955, **20**, 1086) record m. p. 136–138°. ⁷ Found: Cl, 26.4. Required: Cl, 26.6%. ⁸ Found: H₂O, 6.5. Required: H₂O, 6.9%. ⁹ Found: P, 9.3; H₂O, 4.8. Required: P, 8.7; H₂O, 5.2%. ¹⁰ Found: Cl, 13.9. Required: Cl, 13.7%. ¹¹ Found: Cl, 24.3. Required: Cl, 24.1. ¹² Found: H₂O, 2.8%. ¹³ Found: Cl, 22.5. Required: Cl, 22.8%. ¹⁴ Found: P, 7.7; H₂O, 2.1. Required: P, 7.9; H₂O, 2.5%. This compound showed weak bands at 1608 and 1515 cm.^{-1} , probably due to $\nu(\text{C}=\text{N})$ and $\nu(\text{N} \rightarrow \text{O})$, respectively. After drying at 100°/15 mm. over P₂O₅ for 3 hr., the H₂O band at 3500 cm.^{-1} disappeared but there was no increase in the intensity of the bands at 1608 and 1515 cm.^{-1} , indicating that the hydrated product is not a secondary hydroxylamine which would arise by 1,3-addition of water to $-\text{CH}=\text{N}(\text{O})-$ group (cf. ref. 12). ¹⁵ Found: Cl, 22.1. Required: Cl, 22.4. ¹⁶ Two bands of equal intensity are observed and the $\text{C}=\text{N}$ absorption cannot be assigned with certainty. ¹⁷ Plates. ¹⁸ Rhombs.

thiols, or potassium ferrocyanide. Infrared spectra of a number of nitrones (see Table) show strong $\nu(\text{N}\rightarrow\text{O})$ and $\nu(\text{C}=\text{N})$ bands at 1555—1534 and 1613—1582 cm^{-1} , respectively, although the latter assignment is subject to uncertainty in view of the presence of benzene-ring absorptions in the region 1600—1580 cm^{-1} . 5-Hydroxy-*n*-pentylidenemethylamine *N*-oxide absorbs at 1515 ($\text{N}\rightarrow\text{O}$) and 1667 ($\text{C}=\text{N}$) cm^{-1} .⁶ The phenylhydroxylamine-glucuronolactone product shows no band between 1500 and 1600 cm^{-1} , indicating the absence of the $\text{N}\rightarrow\text{O}$ group, and a band observed at 1603 cm^{-1} may well be due to a benzene-ring vibration; absorption at 1763 cm^{-1} indicates the presence of a lactone-carbonyl group, and one at 3378 cm^{-1} , due to the *N*-hydroxyl group, indicates it to be a secondary hydroxylamine; in hot *N*-hydrochloric acid, it gives *o*- and *p*-aminophenol and glucuronic acid; in hot *N*-sodium hydroxide, azoxybenzene and sodium glucuronate are obtained. Glucose, galactose, ribose, and rhamnose probably react similarly with phenylhydroxylamine, to give secondary hydroxylamines. Hydroxylamine forms similar adducts with chloral and dichloroacetaldehyde,⁷ and phenylhydroxylamine does so with 2-bromobut-2-enal.⁸ Acetobromoglucose and phenylhydroxylamine yield *N*-phenyl-*N*-(tetra-*O*-acetylglucosyl)hydroxylamine.⁹

In view of the carcinogenicity of 4-nitroquinoline *N*-oxide¹⁰ and arylhydroxylamines,¹¹ some nitrones might be carcinogenic.

Experimental.—Infrared spectra were recorded with a Perkin-Elmer Infracord spectrometer model 137, the samples being in the form of Nujol mulls between rock-salt plates. The other spectra were obtained by using a Perkin-Elmer 120 instrument.

Paper chromatography. Descending chromatography on Whatman No. 1 filter paper in the following solvents was employed: (A) butan-1-ol-propan-1-ol-ammonia (2*N*) (2:1:1); (B) butan-1-ol-acetic acid-water (2:1:1); (C) ethyl acetate-pyridine-water (12:5:4) and (D) butan-1-ol-propan-2-ol-water (1:7:2). Detecting reagents were (i) 1% 4-dimethylamino-cinnamaldehyde in ethanol-6*N*-hydrochloric acid (1:1) for nitrones, hydroxylamines, and aminoaryl derivatives, (ii) dichromate-silver nitrate¹² for sulphides, and (iii) aniline-diphenylamine¹³ for sugar derivatives.

1-Deoxy-1-(*N*-hydroxy-*N*-phenylamino)-*D*-glucuronolactone. A solution of phenylhydroxylamine (1 g.) in 50% aqueous ethanol (20 ml.) containing dissolved glucuronolactone (1.7 g.), after 16 hr. at 0°, deposited colourless needles (2.2 g., from ethanol), m. p. 106° (decomp.), of the *hydroxyamino-sugar* (Found: C, 53.6; H, 4.9; N, 5.1. $\text{C}_{12}\text{H}_{15}\text{NO}_6$ requires C, 53.9; H, 4.9; N, 5.2%). The compound was insoluble in water, ether, chloroform, or benzene, but soluble in dioxan or hot ethanol, and gave a brown colour with ethanolic 1% ferric chloride and a purple colour with hot aqueous 5% potassium ferrocyanide. The compound (0.8 g.) was kept in *N*-sodium hydroxide (5 ml.) for 3 hr. at 20°, then diluted with ethanol (10 ml.), yielding sodium glucuronate (0.2 g.), m. p. and mixed m. p. 150—152° (decomp.); an ether extract of the mother-liquor, after drying (Na_2SO_4) and evaporation, yielded azoxybenzene (0.08 g.; from aqueous ethanol), m. p. and mixed m. p. 36°. In *N*-hydrochloric acid at 80° for 10 min., it gave *o*- (R_F in solvent A, 0.79) and *p*-aminophenol (R_F 0.70).

General preparation of nitrones. For preparation of the compounds listed in the Table equimolar solutions of arylhydroxylamine and aldehyde in the minimum volume of ethanol or aqueous ethanol were kept at 20° in the dark for 6 hr. When no precipitate was formed the solution was diluted with water until milky, warmed slightly to give a clear solution, and stored overnight at 0°. *Products* precipitated were recrystallised to constant m. p. from ethanol or aqueous ethanol.

Reaction of phenylhydroxylamine with aldoses. Solutions of phenylhydroxylamine (0.1 g.) and the following aldoses (0.1 g.) in 50% aqueous ethanol (5 ml.) were kept at 20° for 14 hr.

⁶ Ulrich and Sayigh, *Angew. Chem.*, 1962, **74**, 468.

⁷ Hantzsch, *Ber.*, 1892, **25**, 701; Oddo and Deleo, *Ber.*, 1936, **69**, 287.

⁸ Utzinger and Regenass, *Helv. Chim. Acta*, 1954, **37**, 1892.

⁹ Utzinger, *Annalen*, 1944, **556**, 50.

¹⁰ Nakahara, Fukuoka, and Sugimura, *Gann*, 1957, **48**, 124

¹¹ Boyland, Dukes, and Grover, *Brit. J. Cancer*, in the press.

¹² Knight and Young, *Biochem. J.*, 1958, **70**, 111.

¹³ Harris and MacWilliam, *Chem. and Ind.*, 1954, 249.

[the R_F values of the adducts are given in parentheses after each sugar for solvents (C) and (D), respectively]: (a) glucose (0.69 and 0.78); (b) galactose (0.66 and 0.60); (c) ribose (0.81 and 0.73); and (d) rhamnose (0.86 and 0.76). All gave purple colours with reagent (i); the products from (a) and (b) gave blue, and from (c) and (d) grey-brown colours with reagent (iii). The reaction mixtures were extracted with ether (3 × 5 ml.) to remove phenylhydroxylamine and its decomposition products, and the aqueous fractions treated with 5% aqueous potassium ferrocyanide (0.2 ml.) and heated at 70° for 15 min.: they gave purple colours.

Reaction of nitrones with thiols. Solutions of the following compounds (0.05 g.) in 50% aqueous ethanol (3 ml.) were treated with cysteine hydrochloride (0.05 g.) in water (1 ml.), or with *N*-acetylcysteine (0.05 g.) in 50% aqueous acetic acid (1 ml.): (a) 4-chloro-, (b) 2,4-dichloro-, (c) 5-hydroxy-2-nitro-, (d) 4-nitro-, and (e) 2-nitro-benzylideneaniline *N*-oxide. Also treated similarly were the products from phenylhydroxylamine and (f) 4-dimethylaminocinnamaldehyde, (g) pyridoxal 5'-phosphate (0.01 g.), and (h) glucuronolactone. After 2 hr. at 60° and 24 hr. at 20°, all the solutions, except (f), containing cysteine hydrochloride showed the presence of *S-p*-aminophenylcysteine (R_F in solvent A 0.33, in B 0.71) and those containing *N*-acetylcysteine, except (f), gave *p*-aminophenylmercapturic acid (R_F in A 0.20, in B 0.67). Both products gave the colour reactions described by Boyland *et al.*³

Reaction of nitrones with benzaldehydes. Solutions of the following (0.05 g.) in ethanol (2 ml.) were heated with *o*-phthalaldehydic acid (0.05 g.) in ethanol (2 ml.) at 65° for 5 hr.: (a) benzylideneaniline *N*-oxides: 2-hydroxy-, 2- and 4-nitro-, 2- and 4-chloro-, 5-hydroxy-2-nitro-, and 4-dimethylamino-; (b) benzylidene-3,4-dimethylaniline *N*-oxides: 2-hydroxy-, 2- and 4-nitro-, 2,4-dichloro-, and 4-dimethylamino-. Also treated similarly were the products from phenylhydroxylamine and (c) pyridoxal 5'-phosphate (2 mg.) and (d) glucuronolactone. Solutions (a), (c), and (d) gave 2-carboxybenzylideneaniline *N*-oxide [R_F in A 0.32; mauve with reagent (i)]; solution (b) gave 2-carboxybenzylidene-3,4-dimethylaniline *N*-oxide [R_F in A 0.60; mauve with reagent (i)]. A solution of 2-hydroxybenzylideneaniline *N*-oxide (1 g.) in ethanol (25 ml.) was heated at 60° for 2.5 hr. with *p*-nitrobenzaldehyde and, on cooling, deposited 4-nitrobenzylideneaniline *N*-oxide (1 g.), m. p. and mixed m. p., 190° (decomp.). Similar treatment of the glucuronolactone product (1 g.) gave 4-nitrobenzylideneaniline *N*-oxide (0.85 g.) and of 4-chloro-, 2-hydroxy- and 2,4-dihydroxybenzylidene-3,4-dimethylaniline *N*-oxides (1 g. each) gave 3,4-dimethyl-4-nitrobenzylideneaniline *N*-oxide, m. p. and mixed m. p. 163° (decomp.), in >80% yield.

We thank Dr. R. L. Jones (of this Institute) for running and interpreting the infrared spectrograms. This investigation has been supported by grants to this Institute from the Medical Research Council, the British Empire Cancer Campaign, the Anna Fuller Fund, and the National Cancer Institute of the National Institutes of Health, U.S. Public Health Service.

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579. *The Formation of Dialkylformamides in the Oxidation of Secondary Amines with Hydrogen Peroxide.*

By A. A. R. SAYIGH and H. ULRICH.

AQUEOUS hydrogen peroxide oxidises aliphatic secondary amines to the corresponding hydroxylamines.¹ The reducing properties of such compounds, formed in the presence of a strong oxidising agent, account for the low yields generally obtained. When we synthesised a number of new *NN*-dialkylhydroxylamines by this method we found that each crude product showed a strong infrared absorption at 6 μ , which is not seen when they are synthesised by thermal decomposition of tertiary amine oxides² and must be due to a by-product in which there is a C=O or C=N double bond.

¹ Mamlock and Wolfenstein, *Ber.*, 1901, **34**, 2500.

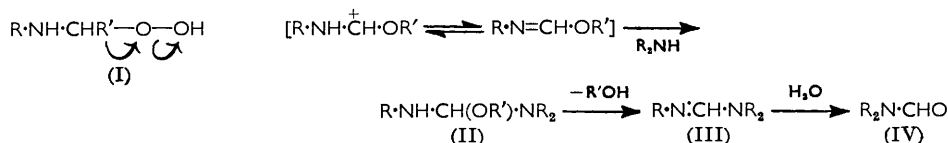
² Mamlock and Wolfenstein, *Ber.*, 1900, **33**, 159; Cope *et al.*, *J. Amer. Chem. Soc.*, 1949, **71**, 3929, and subsequent papers.

From crude *NN*-bis-2-methoxyethylhydroxylamine was isolated a compound $C_7H_{15}NO_3$, shown by infrared evidence to be neither a nitron nor a monosubstituted amide, and identified as *N*-formyldi-2-methoxyethylamine (IV, $R = C_2H_4 \cdot OMe$) by comparison with a sample prepared from di-2-methoxyethylamine and chloral, by the method of Blicke and Chi-Jung Lu.³ These authors report that dialkylformamides are reduced by lithium aluminium hydride to the corresponding dialkylmethylamines and, in agreement with this, we identified the reduction product from our by-product as di-2-methoxyethylmethylamine.

Similarly, oxidation of di-2-ethoxyethylamine gave *N*-formyldi-2-ethoxyethylamine (5%), hexahydroazepine gave *N*-formylhexahydroazepine, and diethylamine gave *N*-formyldiethylamine. Thus the reaction appears to be a general one.

Since no *N*-formyl derivative was formed and the starting material was recovered almost quantitatively when bis-2-ethoxyethylhydroxylamine was treated with hydrogen peroxide, hydroxylamines are not intermediate in the production of the *N*-formyl compounds.

The formation of these unexpected by-products (IV) can be explained by initial formation of the hydroperoxide (I) which concertedly undergoes Baeyer-Villiger rearrangement and attack by the starting secondary amine to give an intermediate (II), which by elimination of $R'OH$ to give a formamidine (III) and subsequent hydrolysis gives the by-products (IV).



Experimental.—Analyses are by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.; infrared absorption spectra were determined by using a Perkin-Elmer model 21 spectrophotometer.

Oxidation procedure. 35% Hydrogen peroxide was added dropwise, with stirring, to an equimolecular amount of secondary amine in ~50% aqueous solution at 55–60°.

NN-Bis-2-methoxyethylhydroxylamine. The mixture from the oxidation of bis-2-methoxyethylamine was set aside overnight and then extracted with benzene. Fractional distillation of the extract gave crude *NN*-bis-2-methoxyethylhydroxylamine (15.8%), b. p. 62°/0.1 mm., n_D^{24} 1.4389. A solution of this material in a slight excess of concentrated hydrochloric acid was extracted with benzene. The acidic solution was neutralised by addition of sodium carbonate and extracted with ethylene chloride. Distillation of the extract gave the pure hydroxylamine, b. p. 64°/0.4 mm., n_D^{24} 1.4372 (Found: C, 48.3; H, 10.1; N, 9.5. $C_8H_{16}NO_3$ requires C, 48.3; H, 10.1; N, 9.4%).

N-Formylbis-2-methoxyethylamine. (a) The benzene extract of the acidic solution of the preceding crude hydroxylamine was dried and distilled to give *N*-formylbis-2-methoxyethylamine (5% based on starting amine), b. p. 80–82°/0.8 mm., n_D^{24} 1.4469 (Found: C, 52.25; H, 9.5; N, 8.9. $C_7H_{15}NO_3$ requires C, 52.15; H, 9.4; N, 8.7%). (b) Chloral (14.75 g., 0.1 mole) was added dropwise with stirring and cooling to bis-2-methoxyethylamine (13.3 g., 0.1 mole). The mixture was stirred for 0.5 hr. at 0° and for 1.5 hr. at room temperature and then distilled, to give the amide (13.7 g., 85%), b. p. 96°/1.9 mm., n_D^{24} 1.4482.

Bis-2-methoxyethylmethylamine. To lithium aluminium hydride (0.5 g.) in tetrahydrofuran (10 ml.) was added *N*-formylbis-2-methoxyethylamine (1.2 g.) in tetrahydrofuran (5 ml.), and the mixture was heated under reflux for 5 hr. Water (0.7 ml.) was then added with ice-cooling. The mixture was extracted with ether and the dried extract saturated with dry hydrogen chloride to cause the separation of the amine hydrochloride as an oil. The ether was decanted and the oil dissolved in a small amount of water. This solution was neutralised by addition of sodium carbonate and extracted with ether. Evaporation of the ether left a residue of bis-2-methoxyethylmethylamine (0.8 g., 73%), which was purified by gas-liquid

³ Blicke and Chi-Jung Lu, *J. Amer. Chem. Soc.*, 1952, **74**, 3933.

chromatography (Found: C, 57.3; H, 11.5; N, 9.7. $C_7H_{17}NO_2$ requires C, 57.1; H, 11.6; N, 9.5%).

NN-Bis-2-ethoxyethylhydroxylamine. The mixture from the oxidation of bis-2-ethoxyethylamine was kept until the exothermic reaction had stopped and then fractionally distilled. Crude *NN-bis-2-ethoxyethylhydroxylamine* was obtained (24%; b. p. 77—79°/0.2 mm., n_D^{22} 1.4382). The *hydrogen oxalate* had m. p. 91—92° (from ethyl acetate) (Found: N, 5.5. $C_{10}H_{21}NO_7$ requires N, 5.2%). Decomposition of this salt yielded pure *NN-bis-2-ethoxyethylhydroxylamine* b. p. 75°/0.03 mm., $n_D^{24.5}$ 1.4352 (Found: C, 54.6; H, 10.9; N, 7.95. $C_8H_{19}NO_3$ requires C, 54.2; H, 10.8; N, 7.9%).

N-Formylbis-2-ethoxyethylamine. (a) The crude *NN-bis-2-ethoxyethylhydroxylamine* was dissolved in acid and this solution was extracted with benzene. Distillation of the extract gave *N-formylbis-2-ethoxyethylamine* (5.5%), b. p. 90—91°/0.3 mm., n_D^{24} 1.4426. (b) Chloral (14.75 g., 0.1 mole) was added dropwise with stirring and ice-cooling to bis-2-ethoxyethylamine (16.1 g., 0.1 mole). Distillation of the mixture yielded *N-formylbis-2-ethoxyethylamine* (15.6 g., 83.5%), b. p. 98—100°/1.0 mm., n_D^{24} 1.4428 (Found: N, 7.5. $C_9H_{19}NO_3$ requires N, 7.4%).

NN-Diethylhydroxylamine. Diethylamine was oxidised as described and after the exothermic reaction had stopped the mixture was saturated with sodium chloride and extracted with methylene chloride. Distillation of the extract gave *NN-diethylhydroxylamine* (40%), b. p. 76°.

N-Formyldiethylamine. Further distillation of the crude product from the oxidation of diethylamine gave *N-formyldiethylamine* (3%), b. p. 92—96°/50 mm., n_D^{23} 1.4355 (lit.,³ b. p. 73°/19 mm., n_D^{20} 1.4346), whose infrared spectrum was superimposable on that of a sample prepared from chloral and diethylamine.³

N-Hydroxyhexahydroazepine. Hexamethyleneimine was oxidised with hydrogen peroxide, and the mixture was left overnight, then extracted with methylene chloride. The extract was distilled to give *N-hydroxyhexahydroazepine* (20.5%), b. p. 64—65°/1.4 mm., n_D^{25} 1.4852 (lit.,⁴ b. p. 94—95°/13 mm.).

N-Formylhexahydroazepine. This was synthesised (83%) from chloral and hexamethyleneimine³ and had b. p. 102—103°/5 mm., n_D^{25} 1.4886 (lit.,⁵ b. p. 127—130°/23 mm., n_D^{20} 1.4903). Gas-liquid chromatography in an Aerograph model A-90, with a column packing of Carbowax on firebrick, at 175° and a flow rate of helium of 10 ml./7 sec., showed it to have a retention time of 525 sec. When the crude *N-hydroxyhexahydroazepine* was analysed under the same conditions it was seen to contain a fraction of the same retention time.

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⁴ Rogers, *Nature*, 1956, **177**, 128.

⁵ Reppe *et al.*, *Annalen*, 1953, **582**, 1.

580. *The Reaction of o-Tolylformamide with Carbonyl Chloride.*

By A. A. R. SAYIGH and H. ULRICH.

'ONIUM CHLORIDES $>N=CHCl]^+Cl^-$ are formed in high yield by the reaction of disubstituted formamides with carbonyl chloride,¹ and if monosubstituted formamides react similarly the corresponding imino-compound $R\cdot N=CHCl$ or its hydrochloride would be expected. These compounds are indeed formed in high yield by reaction of *N*-alkylcarboxamides and carbonyl chloride.^{2,3} There is evidence, in the isolation of isocyanides as major products, that such compounds may be intermediates in the reaction of monosubstituted formamides with phosphorus oxychloride,⁴ cyanuric chloride,⁵ and carbonyl chloride⁶ in

¹ Eillingsfeld, Seefelder, and Weidinger, *Angew. Chem.*, 1960, **72**, 836.

² Unpublished results in this Laboratory.

³ Ugi, Beck, and Fetzer, *Chem. Ber.*, 1962, **95**, 126.

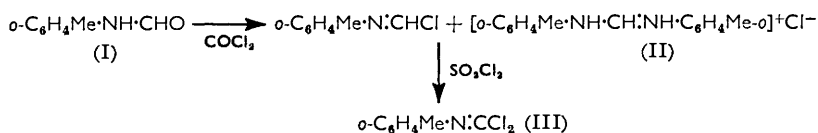
⁴ Ugi and Meyr, *Angew. Chem.*, 1958, **70**, 702.

⁵ Wittmann, *Angew. Chem.*, 1961, **73**, 219.

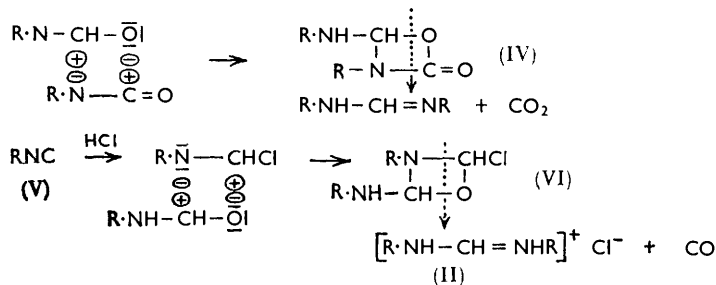
⁶ Ugi, Betz, Fetzer, and Offermann, *Chem. Ber.*, 1961, **94**, 2814.

the presence of a base. In absence of a hydrogen chloride scavenger, monosubstituted formamides and thionyl chloride give complex mixtures.⁷

A solution of *o*-tolylformamide (I) in ethylene dichloride reacted instantly with carbonyl chloride at room temperature. The infrared absorption band (6.05 μ) due to the C=N double bond moved rapidly to 5.93 μ , indicating that unstable intermediate products must be involved. Evaporation under reduced pressure gave a foam from which a 30–36% yield of *NN'*-di-*o*-tolylformamidinium hydrochloride (II) was isolated. When *o*-tolylformamide was added to an excess of carbonyl chloride, 30% of the salt (II) was again obtained.



Since the intermediate was too unstable to be isolated, we attempted its direct chlorination with sulphuryl chloride. If the intermediate is assumed to be *o*-C₆H₄Me·N=CHCl, this reaction would yield the stable *N*-dichloromethylene-*o*-toluidine (III). The feasibility of such a scheme was demonstrated by Kühle,⁸ who chlorinated arylformamides in an excess of thionyl chloride with sulphuryl chloride to obtain such compounds. When we treated the mixture from the reaction of equivalent amounts of *o*-tolylformamide and carbonyl chloride with sulphuryl chloride, the major product was the formamidinium chloride (II) (47%), along with 32.4% of the compound (III). This showed that the compound R·N·CHCl and not the formamidinium, was the most likely precursor of the product (III).



To account for formation of the salt (II) one might postulate that the formamide (I) and carbonyl chloride produce an isocyanate, which with more of the formamide give the four-membered ring intermediate (IV) from which the product could arise by loss of carbon dioxide. This was discounted when no formamidinium was isolated on reaction of the formamide (I) and *o*-tolyl isocyanate in the presence of hydrogen chloride. Next, *o*-tolyl isocyanide (V; R = *o*-C₆H₄Me) was synthesised from the formamide and carbonyl chloride in the presence of triethylamine (cf. Ugi *et al.*⁶); the yield was 31.7%, in accord with the 32.4% of compound (III) obtained in the sulphuryl chloride experiment. An equimolar mixture of the formamide (I) and isocyanide (V) in ethylene dichloride was treated with gaseous hydrogen chloride; the formamidinium salt (II) was produced, showing that this path for the reaction mechanism is possible. Again we envisage a four-membered ring intermediate (VI), formed by dipolar addition. The original, transient C=N absorption at 6.05 μ could therefore be due to the intermediate R·N·CHCl. The mechanism has analogy in the reaction of aryl isocyanates with dimethylformamide, which afforded *N*-aryl-*NN'*-dimethylformamidines.⁹

⁷ Vaughan and Carlson, *J. Amer. Chem. Soc.*, 1962, **84**, 769.

⁸ Kühle, G.P. 1,094,737.

⁹ Jovtscheff and Falk, *J. prakt. Chem.*, 1961, **13**, 265.

It can be concluded, then, that in the reaction of *o*-tolylformamide and carbonyl chloride, the imide $R \cdot N : CHCl$ is an intermediate, its presence being indicated by its conversion into the isocyanide (V) and dichloro-compound (III); the intermediate competes with carbonyl chloride for the starting *o*-tolylformamide, with which it reacts to form di-*o*-tolylformamidinium chloride. Since this product is obtained in the same yield whether the *o*-tolylformamide or carbonyl chloride is in excess, the rates of the competing reactions are fairly similar.

Experimental.—Analyses are by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.; infrared absorption spectra were determined by a Perkin-Elmer model 21 spectrophotometer.

Reaction of o-tolylformamide with carbonyl chloride. To a solution of *o*-tolylformamide (13.5 g., 0.1 mole) in ethylene dichloride (50 ml.) was added carbonyl chloride (10.7 g., 0.108 mole) in ethylene dichloride (50 ml.) during 30 min. (temp., 26–37°), to give a clear, yellow-to-orange solution, which showed an intense absorption at 6.05 μ . The mixture was heated at 75–80° and the unchanged carbonyl chloride was removed in a stream of nitrogen. During the heating the colour of the mixture darkened to red-brown, and a shift of the infrared absorption to 5.93 μ was observed. The solvent was evaporated to give a gummy residue (16.7 g.), which, on trituration with acetone, afforded NN'-di-*o*-tolylformamidinium chloride (II) (4.7 g., 36%), m. p. 219–220° (from acetone) (Found: C, 69.1; H, 6.55; Cl, 13.5; N, 11.0. $C_{15}H_{17}ClN_2$ requires C, 69.1; H, 6.6; Cl, 13.6; N, 10.7%).

A sample of the hydrochloride was converted into NN'-di-*o*-tolylformamide, m. p. 152° (lit.,¹⁰ m. p. 151°).

When the *o*-tolylformamide was added to the carbonyl chloride, 30% of the same salt (II) was isolated.

Reaction of o-tolylformamide with carbonyl chloride in the presence of triethylamine. Carbonyl chloride (10 g., 0.1 mole) was added dropwise, in 36 min., to *o*-tolylformamide (13.5 g., 0.1 mole) and triethylamine (20.2 g., 0.2 mole) in benzene (85 ml.), the temperature rising from 8° to 26°. After a further 30 min., triethylamine hydrochloride (27.5 g., 100%) was filtered off, and the benzene was removed under reduced pressure. The residue (11.9 g.) was distilled, to give *o*-tolyl isocyanide (V; $R = o-C_6H_4Me$) (3.7 g., 31.7%), b. p. 58–59°/7 mm., λ_{max} (in $CHCl_3$) 3.38, 4.70, 6.70, 6.81, and 9.00 μ .

Reaction of o-tolylformamide with carbonyl chloride and sulphuryl chloride. Carbonyl chloride (11.1 g., 0.112 mole) in ethylene dichloride (50 ml.) was added in 38 min. to a solution of *o*-tolylformamide (14.85 g., 0.11 mole) in ethylene dichloride (50 ml.) at 21–31°. The mixture was cooled to 2° and sulphuryl chloride (14.85 g., 0.11 mole) was added with cooling. After 20 hours' stirring at room temperature, a stream of nitrogen was passed through the solution at 40–45° for 45 min. The solvent was evaporated and the residue treated with ether (100 ml.), to give the salt (II) (6.7 g., 47%). When the ether was evaporated, a residue (9.5 g.) was obtained, which on distillation under reduced pressure yielded *N*-dichloromethylene-*o*-toluidine (III) (6.1 g., 32.4%), b. p. 58–68°/0.4 mm., λ_{max} (in $CHCl_3$) 6.05 and 11.15 μ .

o-Tolylformamide and o-tolyl isocyanate in the presence of hydrogen chloride. *o*-Tolyl isocyanate (1.25 g., 0.01 mole) was added to *o*-tolylformamide (1.35 g., 0.01 mol.) in ethylene dichloride (15 ml.). Examination of the infrared spectrum of the mixture showed that no reaction took place. Hydrogen chloride was bubbled into the reaction mixture and the observable change was the formation of *o*-tolylcarbonyl chloride.

Reaction of o-tolylformamide and o-tolyl isocyanide in the presence of hydrogen chloride. *o*-Tolylformamide (1.35 g., 0.01 mole) was added to a solution of *o*-tolyl isocyanide (1.17 g., 0.01 mole) in ethylene dichloride (13.5 ml.). Dry hydrogen chloride was added to this mixture until the exothermic reaction stopped. After passage of nitrogen the solvent was evaporated, giving a residue (4.1 g.) which, on treatment with benzene, yielded the salt (II) (0.8 g., 30.7%), m. p. 213°. The infrared spectrum of this material was superimposable on that of material (II) obtained as above.

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¹⁰ Nef, *Annalen*, 1892, **270**, 312.

581. *Transition-metal Complexes of Triethylenetetramine. Part I.*
Nickel(II) and Copper(II) Tetrachlorozincates.

By D. A. HOUSE and N. F. CURTIS.

In an investigation of the reactions between carbonyl groups and co-ordinated polydentate aliphatic amine ligands¹ it was necessary to prepare crystalline derivatives of the quadridentate ligand, *NN'*-di-(2-aminoethyl)ethylenediamine (triethylenetetramine = trien) with several transition-metal ions. Although much information is available on the stability of the complex ions of this ligand in solution,² data on the isolation and characterisation of crystalline complexes are generally lacking. Basolo,³ and Searle and Sargenson⁴ prepared complexes of this ligand with cobalt(III), and Jonassen and his co-workers^{5,6} the compounds $[\text{Ni}_2(\text{trien})_3]\text{Cl}_4 \cdot 2\text{H}_2\text{O}$, $[\text{Pd trien}]\text{PdCl}_4$, and $[\text{Pt trien}]\text{PtCl}_4$. Water-insoluble precipitates of $[\text{Ni trien}]\text{AgBrI}$ and $[\text{Ni trien}](\text{SCN})_2$ have been obtained by Jørgensen.⁷ The only crystalline compound previously reported with copper(II) and triethylenetetramine is the water-unstable $[\text{H}_4 \text{ trien}]\text{CuCl}_6$ with copper(II) in the anion.⁸

We here describe the preparation and properties of $[\text{Ni trien}]\text{ZnCl}_4 \cdot \text{H}_2\text{O}$, $[\text{Ni trien}]\text{ZnCl}_4$, $[\text{Cu trien}]\text{ZnCl}_4 \cdot \text{H}_2\text{O}$, and $[\text{Cu trien}]\text{ZnCl}_4$. The compound $[\text{Ni trien}]\text{ZnCl}_4 \cdot \text{H}_2\text{O}$ forms, from water, pale blue crystals which become orange at 110°. Weight-loss and analytical and infrared results correspond to the formula $[\text{Ni trien}]\text{ZnCl}_4$ for this orange compound. It is quite stable if stored over silica gel, but reverts to the blue hydrate in air. The blue-to-orange transition on loss of water is analogous to a similar change with di(ethylenediamine)nickel(II) perchlorate dihydrate, which changes from blue to orange, to form the anhydrous diamagnetic salt. The orange salt $[\text{Ni trien}]\text{ZnCl}_4$ is also diamagnetic. The hydrate is very soluble in water, giving a blue solution which becomes yellow when heated. This blue-yellow transition of the $[\text{Ni trien}]^{2+}$ ion in aqueous solution has been studied spectroscopically by Jørgensen.⁷ The orange salt $[\text{Ni trien}]\text{ZnCl}_4$ is also soluble in water, giving a blue solution. Both salts are insoluble in methanol and ethanol.

The hydrate $[\text{Cu trien}]\text{ZnCl}_4 \cdot \text{H}_2\text{O}$ is formed as deep violet-black crystals from aqueous solutions. Heating at 110° causes a weight loss corresponding to loss of one molecule of water, giving the salt $[\text{Cu trien}]\text{ZnCl}_4$, which slowly reverts to the hydrate in air. The anhydrous compound has a deeper violet colour than the hydrate, and both are readily soluble in water, giving deep blue solutions of the $[\text{Cu trien}]^{2+}$ ion. The visible absorption spectra in aqueous solution corresponds to that previously reported for this ion.^{9,10} Addition of organic solvents, *e.g.*, acetone or alcohols, to the deep blue aqueous solution shifts the 576 μ absorption peak towards the red, and the solution becomes violet. Both the copper(II) compounds are insoluble in acetone, methanol, and ethanol.

The infrared spectra of the hydrates show bands due to co-ordinated water at 3430 and 1630 cm^{-1} for the nickel compound, and at 3420 and 1625 cm^{-1} for the copper analogue. These bands are absent in spectra of the anhydrous compounds. All four compounds show bands due to the NH_2 group at about 3353 and 1585 cm^{-1} and a band at 3135 cm^{-1} due to the NH group.

¹ House and Curtis, *J. Amer. Chem. Soc.*, 1962, **84**, 3248.

² Sillén and Schwarzenbach, "Stability Constants, Part I, Organic Ligands," *Chem. Soc. Special Publ.* No. 6, 1957, p. 42.

³ Basolo, *J. Amer. Chem. Soc.*, 1948, **70**, 2634.

⁴ Searle and Sargenson, Paper presented at the pre-ANZAAS Symposium on Co-ordination Chemistry, Aug. 1962, Sydney, Australia.

⁵ Jonassen and Douglas, *J. Amer. Chem. Soc.*, 1949, **71**, 4094.

⁶ Jonassen and Cull, *J. Amer. Chem. Soc.*, 1949, **71**, 4097.

⁷ Jørgensen, *Acta Chem. Scand.*, 1957, **11**, 399.

⁸ Jonassen, Crumpler, and O'Brien, *J. Amer. Chem. Soc.*, 1945, **67**, 1709.

⁹ Pflaum, *J. Amer. Chem. Soc.*, 1954, **76**, 6215.

¹⁰ Kirson, *Bull. Soc. chim. France*, 1957, 1178.

Magnetic susceptibilities, measured for the solid by the Gouy method with tri(ethylenediamine)nickel(II) thiosulphate as calibrant,¹¹ are tabulated.

Magnetic susceptibilities.						
Substance	Mol. wt.	Temp. (K)	$10^6\chi_M$	$10^6\chi_d$	$10^6\chi_{corr.}$	$\mu_{eff.}$ (B.M.)
[Cu trien]ZnCl ₄ ·H ₂ O	435	290	2·81	252	1477	1·86
[Ni trien]ZnCl ₄ ·H ₂ O	430	290	8·34	253	3841	3·00
[Ni trien]ZnCl ₄	412			Diamagnetic		

Experimental.—Bis(1,3-diaminopropane)- μ -triethylenetetraminedinickel(II) chloride dihydrate, [Ni₂(trien)₂]Cl₄·2H₂O. The procedure of Jonassen and Douglas⁵ was modified slightly as large quantities of this material were required. Nickel(II) chloride hexahydrate (23·7 g., 0·1 mole) was dissolved in 95% ethanol (50 ml.) and triethylenetetramine (22 g., 0·15 mole), diluted with an equal volume of ethanol, was added slowly with stirring. Heat was evolved and, on cooling, mauve-pink crystals of the complex salt were deposited (22–24 g., 60–65%). The product was recrystallised from water–ethanol (Found: C, 29·7; H, 8·4; Cl, 19·2; Ni, 16·4. Calc. for C₁₈H₅₈Cl₄N₁₂Ni₂O₂: C, 29·5; H, 8·0; Cl, 19·3; Ni, 16·1%), λ_{max} . 547 and 348 m μ (ϵ 13 and 19, respectively).

Triethylenetetraminenickel(II) tetrachlorozincate, [Ni trien]ZnCl₄·H₂O. Nickel(II) chloride hexahydrate (5 g., 0·021 mole) and the salt [Ni₂(trien)₂]Cl₄·2H₂O (15·4 g., 0·021 mole) were mixed with methanol (47·5 ml.) and water (2·5 ml.). The mixture was heated under reflux until all the complex had dissolved and the solution was a clear blue (about 30 min.). This solution contained the [Ni trien]²⁺ ion but attempts to isolate the chloride by addition of acetone¹² gave only a blue oil. The blue solution was added dropwise with stirring to a boiling solution of anhydrous zinc chloride (10 g.) in methanol (30 ml.). A yellow solution was formed which, while still warm, deposited fine orange crystals of the anhydrous salt. On cooling, these changed to the blue monohydrate. If the blue [Ni trien]²⁺ solution was made more aqueous, the yellow tetrachlorozincate solution became blue without the intermediate deposition of the orange salt. In this case blue crystals of the monohydrate were obtained on addition of ethanol, cooling, and scratching. The yield of *tetrachlorozincate hydrate* was 18 g. (70% based on the complex used) (Found: C, 16·9; H, 4·8; Cl, 32·8; Ni, 13·8; H₂O, 4·3. C₆H₂₀Cl₄N₄NiOZn requires C, 16·8; H, 4·7; Cl, 32·8; Ni, 13·6; H₂O, 4·2%). The salt had λ_{max} . at room temperature 562 (ϵ 10) and 358 m μ (ϵ 19).

Heating the blue hydrate at 110° for 3 hr. gave the orange anhydrous *salt* (Found: C, 17·5; H, 4·6; Cl, 34·0; Ni, 14·4. C₆H₁₈Cl₄N₄NiZn requires C, 17·5; H, 4·4; Cl, 34·2; Ni, 14·3%).

Triethylenetetraminecopper(II) tetrachlorozincate(II) monohydrate, [Cu trien]ZnCl₄·H₂O. Anhydrous copper(II) chloride (3·3 g., 0·025 mole) was dissolved in water (10 ml.), and triethylenetetramine (3·7 g., 0·025 mole), diluted with ethanol (10 ml.), was slowly added. The deep blue solution was filtered and slowly added to a hot solution of anhydrous zinc chloride (6 g.) in ethanol (50 ml.). Deep violet-black crystals of hydrated *product* were formed on cooling (6·5 g., 60%). These recrystallised from water–ethanol (Found: C, 16·9; H, 4·3; Cl, 32·4; Cu, 14·2; H₂O, 4·1. C₆H₂₀Cl₄CuN₄OZn requires C, 16·6; H, 4·6; Cl, 32·6; Cu, 14·6; H₂O, 4·1%), then having λ_{max} . 255 and 576 m μ (ϵ 5000 and 165 respectively).

Heating the hydrate at 110° for 3 hr. gave the deep blue anhydrous *salt* (Found: C, 17·2; H, 4·4; Cl, 33·8; Cu, 15·0. C₆H₁₈Cl₄CuN₄Zn requires C, 17·2; H, 4·3; Cl, 33·9; Cu, 15·2%).

Spectra. The visible and ultraviolet spectra were determined for aqueous solutions by using a Unicam S.P. 500 spectrophotometer. The infrared spectra were determined for mulls, in a Perkin-Elmer model 221 infrared spectrophotometer.

Analyses. Nickel was determined as its dimethylglyoxime derivative, and copper as the salicylaldehyde complex. The triethylenetetramine complex cations were decomposed by boiling peroxydisulphate solution before analysis. Nitrogen was determined by the Dumas method.

¹¹ Curtis, J., 1961, 3147.

¹² *Inorg. Synth.*, 1960, 6, 198.

The authors thank Mr. R. Woods, of this Department, for the infrared spectral determinations and Dr. A. D. Campbell, of the University of Otago, for carbon, hydrogen, and nitrogen analyses.

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582. Protonation of Hydrazine Derivatives.

By R. F. EVANS and W. KYNASTON.

IN connection with work, now discontinued, on polymers containing the hydrazine moiety we have measured the infrared spectra of the hydrochlorides of hydrazine and of some alkyl and aryl derivatives. We found, from a consideration of the spectra in the NH-stretching region and by application of the band assignments previously worked out for the spectra of hydrazine mono-¹ and di-hydrochloride,² that it was possible to decide which nitrogen atom in the hydrazine derivative had been protonated. Our results are presented in the Table, together with data for hydrazine mono- and di-hydrochloride and 1,1-dimethylhydrazine, which differ slightly from published values.

Characteristic NH stretching absorption bands (cm.⁻¹) * in the infrared spectra of hydrazine hydrochlorides.

Group assignments	NH ₂ or NH		NH ₃ ⁺				NH ⁺		
Hydrazine hydrochloride	3239 (3261)	3150 (3150)	2971 (2950)	Very broad band 3000—2400 with ill-defined maxima. (2908) (2841) (2739) (2674) (2600) †		2697 (2716)	2580		
Hydrazine dihydrochloride									
1,1-Dimethylhydrazine	3308 (3298)	3223 ‡ (3126)	3142 (3126)						
1,1-Dimethylhydrazine hydrochloride	3239	3131			2726	2676	2632	2519	2484
1,1-Di-isopropylhydrazine hydrochloride	3260	3150				2668	2565	2524	2422
Phenylhydrazine hydrochloride		3206	2943			2843m	2691		
1,1-Diphenylhydrazine hydrochloride		3158w	3081w	2896			2685		

* All bands are very intense unless otherwise stated. Values in parentheses refer to published data. † Measured at -180°. ‡ Probably overtone of a fundamental near 1600 cm.⁻¹.

The spectrum of 1,1-dimethylhydrazine in the liquid state possesses three strong bands above 3100 cm.⁻¹, two of which have been assigned to the NH stretching vibrations of an amino-group.³ In the spectrum of 1,1-dimethylhydrazine hydrochloride there are still two bands above 3100 cm.⁻¹, but they have been displaced by 70—90 cm.⁻¹ towards lower frequencies. In addition, four new strong bands have appeared between 2726 and 2484 cm.⁻¹.



If the proton is assumed to go completely on to one nitrogen atom, the two possible structures for the cation of 1,1-dimethylhydrazine hydrochloride are (I and II; R' = R'' = Me). In structure (II) the NH stretching vibrations will refer to one group only, the

¹ Decius and Pearson, *J. Amer. Chem. Soc.*, 1953, **75**, 2436.

² Snyder and Decius, *Spectrochim. Acta*, 1959, **13**, 280.

³ Shull, Wood, Aston, and Rank, *J. Chem. Phys.*, 1954, **22**, 1191.

NH_3^+ group. The highest value for the NH stretching frequency of the NH_3^+ group in hydrazine hydrochloride is 2971 cm^{-1} ; in hydrazine dihydrochloride it is 2908 cm^{-1} , and even in methylamine hydrochloride it is only 3075 cm^{-1} .⁴ Hence structure (II) is debarred since it cannot account for the two strong bands above 3100 cm^{-1} .

In structure (I), however, the NH stretching bands will be of two types, those belonging to the NH^+ grouping and those belonging to the NH_2 group. The latter should give rise to two strong NH stretching vibration bands above 3100 cm^{-1} but, since a partial positive charge is developed on the nitrogen atom of the NH_2 group owing to the inductive effect of the positive charge on the neighbouring atom, these two bands will occur at frequencies lower than those expected for normal amines. This is found to be the case in the spectrum of 1,1-dimethylhydrazine hydrochloride, and it is significant that the corresponding two bands in the spectrum of hydrazine hydrochloride, which are assigned to NH stretching vibrations of the NH_2 group, appear at substantially the same frequencies as the two bands in 1,1-dimethylhydrazine hydrochloride. In trimethylamine hydrochloride⁴ the NH^+ stretching band is at 2735 cm^{-1} , which strongly supports the assignment of the four strong bands from 2726 to 2484 cm^{-1} in the spectrum of 1,1-dimethylhydrazine hydrochloride to the NH stretching vibrations of the NH^+ group. Hence, structure (I; $\text{R}' = \text{R}'' = \text{Me}$) is the more likely for the cation in 1,1-dimethylhydrazine hydrochloride. Similarly, the infrared spectrum of 1,1-di-isopropylhydrazine hydrochloride strongly supports structure (I; $\text{R}' = \text{R}'' = \text{Pr}$) for the cation.

With phenylhydrazine hydrochloride, the spectrum has only one band above 3100 cm^{-1} . Structure (I; $\text{R}' = \text{Ph}$, $\text{R}'' = \text{H}$) is not applicable because it would give rise to two strong bands in this region. Structure (II; $\text{R}' = \text{Ph}$, $\text{R}'' = \text{H}$) is preferred since not only will it give only one band above 3100 cm^{-1} but also the similarity of the spectrum in the 2943 — 2691 cm^{-1} region to that of hydrazine monohydrochloride, is explained by the presence of the NH_3^+ group.

Similarly, 1,1-diphenylhydrazine hydrochloride gives rise to a cation of structure (II; $\text{R}' = \text{R}'' = \text{Ph}$), since the spectrum shows that there are no strong bands above 3100 cm^{-1} (and hence no NH_2 groups in the molecule), while there are bands in the correct region for NH stretching of the NH_3^+ group.

Alkyl groups, by virtue of their inductive effect, increase the flow of electrons to the nitrogen atom to which they are attached and render it more basic. Phenyl groups, on the other hand, are base-weakening. In the four hydrazine derivatives examined it is seen that the proton has added to the nitrogen atom which, after consideration of the electrical effects of the substituents, is the more basic.

Experimental.—(a) *Materials.* 1,1-Di-isopropylhydrazine hydrochloride was prepared from di-isopropylamine by nitrosation followed by reduction of the *N*-nitroso-derivative.

Sodium nitrite (7.2 g.) in water (15 ml.) was added, during 5 min., to an ice-cold solution of di-isopropylamine (10 g.) in *n*-hydrochloric acid (100 ml.). After storage of the solution at 0° for 30 min., *n*-hydrochloric acid (15 ml.) was added and the solution was kept at room temperature for 1.5 hr. The mixture was distilled and the distillate extracted with ether. Evaporation of the dried (Na_2SO_4) extract yielded *N*-nitrosodi-isopropylamine (5.5 g., 42%), m. p. 45.5 — 47° after one crystallisation from ether-ethanol (Found: C, 55.7; H, 10.4; N, 21.8. Calc. for $\text{C}_6\text{H}_{14}\text{N}_2\text{O}$: C, 55.4; H, 10.8; N, 21.5%).

A slurry of sodium dithionite (14.3 g.) in water (20 ml.) was added to *N*-nitrosodi-isopropylamine (5.5 g.) and sodium hydroxide (30 g.) in water (150 ml.) and ethanol (150 ml.). The mixture was kept at 55 — 60° for 2 hr., refluxed on the steam-bath for 2 hr., and filtered. The filtrate was distilled on the steam-bath, and the distillate diluted with water and extracted with light petroleum (b. p. 40 — 60°). The aqueous layer was made alkaline with concentrated aqueous sodium hydroxide and redistilled. The distillate was acidified with concentrated hydrochloric acid and evaporated to dryness at $100^\circ/20\text{ mm.}$, and the residue was crystallised from ether-propan-1-ol at -15° yielding deliquescent 1,1-di-isopropylhydrazine hydrochloride,

⁴ Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1958, Ch. 14.

m. p. 89—91° (Found: C, 47.1; H, 10.7; Cl, 23.0; N, 18.8. $C_6H_{17}ClN_2$ requires C, 47.2; H, 11.2; Cl, 23.2; N, 18.4%).

1,1-Diphenylhydrazine hydrochloride was available commercially. The remaining hydrochlorides were prepared by addition of the calculated quantity of hydrochloric acid to ethanolic solutions of the free bases, evaporation of the solvents at 100°/30 mm., and drying of the residue over phosphorus pentoxide.

(b) *Spectra*. The infrared spectra of the hydrochlorides were measured as potassium chloride discs on a double-beam recording grating-spectrometer, designed and constructed in this laboratory. The spectrum of 1,1-dimethylhydrazine was measured as a thin capillary-film.

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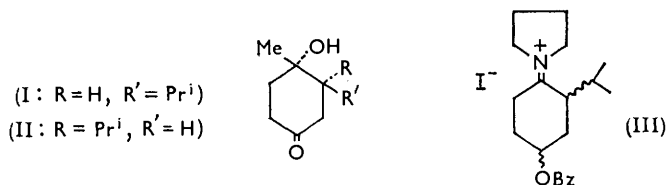
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583. *Reactions of Organic Peroxides. Part III.* The Synthesis of* *(±)-cis- and -trans-4-Hydroxy-3-isopropyl-4-methylcyclohexanone.*

By D. BROWN and T. G. HALSALL.

REDUCTION of ascaridole with ferrous sulphate solution affords¹ two hydroxy-ketones which were shown¹ by degradation, and by synthesis of the corresponding deoxo-compounds, to be (±)-*cis*- (I), m. p. 113.5°, and (±)-*trans*-Me,Prⁱ-4-hydroxy-3-isopropyl-4-methylcyclohexanone (II), m. p. 84°. These ketones have now been synthesised.



The pyrrolidine-enamine of 4-benzoyloxycyclohexanone was heated under reflux with isopropyl iodide, and the resulting *C*-alkylated product (III) hydrolysed to give the isomeric 4-benzoyloxy-2-isopropylcyclohexanones.² These were heated under reflux overnight with 20 mol. of methylmagnesium iodide, to give an oil which was oxidised with chromic acid in acetone.³ Chromatography of the product afforded the two ketones (I) and (II) which were identical with the corresponding ketones from ascaridole.

Experimental.—The alumina used for chromatography was material of activity I—II which had been deactivated with 5% of 10% aqueous acetic acid. M. p.s were determined in capillary tubes.

4-Benzoyloxycyclohexanone. The crude mixture of isomeric 4-benzoyloxycyclohexanols prepared⁴ from a mixture of *cis*- and *trans*-cyclohexane-1,4-diol was oxidised by chromic acid

* Part II, *J.*, 1963, 1095.

¹ Davis, Halsall, and Hands, *Proc. Chem. Soc.*, 1961, 83; Brown, Davis, Halsall, and Hands, *J.*, 1962, 4492.

² Cf. Stork, U.S.P. 2,773,099/1956.

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

⁴ Dendy and Taylor, *J.*, 1957, 1922.

in an ether-water two-phase system.⁵ The product was contaminated with *cis*- (m. p. 127°) and *trans*-1,4-dibenzoyloxycyclohexane (m. p. 152°) and was purified by chromatography on alumina to give 4-benzoyloxycyclohexanone, m. p. 63°.

*Isopropylation of 4-benzoyloxycyclohexanone.*² The ketone (5 g.) was heated under reflux with pyrrolidine (10 c.c.) and dry benzene (50 c.c.) in a Dean and Stark apparatus. After the theoretical quantity (0.4 c.c.) of water had come over, the excess of pyrrolidine and the benzene were distilled off under reduced pressure to give the enamine as a solid. Isopropyl iodide (50 c.c.) was added and the mixture was heated under reflux for 60 hr. Water (40 c.c.) was added and the excess of iodide distilled off. To ensure complete hydrolysis of the salt (III), methanol (40 c.c.) was added and the mixture heated under reflux for 2.5 hr. After the addition of more water (40 c.c.) the mixture was distilled until the b. p. of the distillate reached 100°. Continuous ether-extraction then afforded a yellow solid (4.3 g.). This was absorbed from light petroleum (b. p. 40–60°)–benzene on alumina (250 g.). Elution with light petroleum–benzene (9 : 1) gave the following fractions: (i) the isomeric 4-benzoyloxy-2-isopropylcyclohexanones (0.53 g., 9%) as an oil, $n_D^{20.5}$ 1.5185 (Found: C, 73.95; H, 7.85. Calc. for $C_{16}H_{20}O_3$: C, 73.8; H, 7.85%), ν_{max} (liquid film) 1710 cm^{-1} , (ii) a 3 : 2 mixture (0.28 g.) of the isomeric 4-benzoyloxy-2-isopropylcyclohexanones and 4-benzoyloxycyclohexanone, and (iii) 4-benzoyloxycyclohexanone (2.54 g.). The chromatography was followed by gas-liquid chromatography of the fractions.

(±)-*cis*- and *trans*-Me,Pr¹-4-Hydroxy-3-isopropyl-4-methylcyclohexanone. The mixture of isomeric benzoyloxy-2-isopropylcyclohexanones (0.14 g.) in dry ether (5 c.c.) was added to methylmagnesium iodide (20 ml.) in ether (10 c.c.). After 30 min. more ether (10 c.c.) was added and the mixture was heated under reflux for 18 hr., then decomposed at 0° with water (5 c.c.) which was slowly added. *N*-Hydrochloric acid (10 c.c.) at 0° was then added. Extraction with ether afforded an oil (0.113 g.), ν_{max} (liquid film) 3400 cm^{-1} (OH) which was dissolved in acetone (12 c.c.) at 0°. Chromic acid³ (0.3 c.c.; theor. 0.1 c.c.) was added dropwise. After the orange colour had persisted for 3 min. methanol (1 c.c.) was added to destroy the excess of oxidant. The mixture was worked up in the usual manner to give an oil which was adsorbed from light petroleum (b. p. 40–60°)–benzene on alumina (15 g.). Elution with light petroleum–benzene (3 : 1) removed $\alpha\alpha$ -dimethylbenzyl alcohol from the column. Elution with benzene gave (±)-*trans*-Me,Pr¹-4-hydroxy-3-isopropyl-4-methylcyclohexanone (37 mg., 40%) as needles, m. p. and mixed m. p. with the appropriate hydroxy-ketone from ascaridole, 82–82.5° (Found: C, 70.65; H, 10.6. Calc. for $C_{16}H_{18}O_2$: C, 70.55; H, 10.65%), ν_{max} (in CCl_4) 3570 and 1710 cm^{-1} . Elution with benzene–ether (49 : 1) gave (±)-*cis*-Me,Pr¹-4-hydroxy-3-isopropyl-4-methylcyclohexanone (12 mg., 13%) as plates, m. p. and mixed m. p. with the appropriate ketone from ascaridole, 110.5–111° (Found: C, 70.6. H, 10.7), ν_{max} (in CCl_4) 3570 and 1710 cm^{-1} .

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⁵ Brown and Garg, *J. Amer. Chem. Soc.*, 1961, **83**, 2852.

584. Condensation of Diketones with Aromatic Compounds. Part II.* Condensation of Hexane-2,5-dione with Veratrole and Catechol.

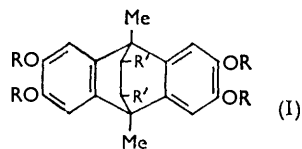
By IRENE M. DAVIDSON and O. C. MUSGRAVE.

A REACTION between veratrole and hexane-2,5-dione in 70% v/v aqueous sulphuric acid was observed some years ago by Drs. A. M. Meston and J. M. C. Thompson¹ in this Department. The product, $C_{22}H_{26}O_4$, m. p. 185°, was shown to contain four methoxyl groups but its structure was not established.

* Part I, Manson and Musgrave, *J.*, 1963, 1011.

¹ A. M. Meston, Ph.D. Thesis, Aberdeen, 1952.

The compound shows ultraviolet absorption resembling closely that of the 9,10-dialkyl-9,10-dihydro-2,3,6,7-tetramethoxyanthracenes² and therefore contains a similar ring system. We have established that it has the structure (I; R = Me, R' = H) by synthesising it from 2,3,6,7-tetramethoxy-9,10-dimethylantracene. This reacted with maleic anhydride forming the adduct (I; R = Me, R'R' = CO·O·CO), the ultraviolet absorption of which indicates that 9,10-addition had occurred. The anthracene reacted in a similar manner with ethylene³ under forcing conditions, to give 9,10-dihydro-2,3,6,7-tetramethoxy-9,10-dimethyl-9,10-ethanoanthracene (I; R = Me, R' = H) which proved to be identical with the veratrole-hexane-2,5-dione product.



The condensation of catechol with hexane-2,5-dione in aqueous sulphuric acid gives a compound $C_{18}H_{18}O_4$ which was thought by Niederl and Nagel⁴ to be an indanoindane derivative. Le Goff⁵ recently suggested that the observed proton magnetic resonance spectrum is best explained by the structure (I; R = R' = H). We have confirmed that this is correct by converting the catechol-hexane-2,5-dione product by methylation into the ethanoanthracene (I; R = Me, R' = H).

Experimental.—Ultraviolet absorption spectra were measured for ethanolic solutions, a Hilger Ultrascan spectrophotometer being used.

Condensation of veratrole with hexane-2,5-dione. Hexane-2,5-dione (45.6 g.) was added dropwise with stirring during $\frac{1}{2}$ hr. to a solution of veratrole (110.4 g.) in 70% v/v aqueous sulphuric acid (1 l.). The mixture was kept for 3 weeks at room temperature and then poured into water (1.5 l.). The resulting solid was collected and crystallised from ethanol, giving 9,10-dihydro-2,3,6,7-tetramethoxy-9,10-dimethyl-9,10-ethanoanthracene (58.0 g.) as plates, m. p. 186.5—187° (Found: C, 74.3; H, 7.4. $C_{22}H_{26}O_4$ requires C, 74.55; H, 7.4%), λ_{max} 2925 Å (log ϵ 4.03), λ_{inf} 2290 Å (log ϵ 4.17).

9,10-Dihydro-2,3,6,7-tetramethoxy-9,10-dimethyl-9,10-ethanoanthracene-11,12-dicarboxylic anhydride. A mixture of 2,3,6,7-tetramethoxy-9,10-dimethylantracene⁶ (0.32 g.) and maleic anhydride (0.14 g.) in benzene (30 ml.) was heated under reflux for 2 hr. Evaporation of the solvent gave the *anhydride* which crystallised from ethyl acetate in plates (0.3 g.), m. p. 240—241° (Found: C, 67.6; H, 5.7. $C_{24}H_{24}O_7$ requires C, 67.9; H, 5.7%), λ_{max} 2930 Å (log ϵ 3.92), λ_{inf} 2320 Å (log ϵ 4.05).

9,10-Dihydro-2,3,6,7-tetramethoxy-9,10-dimethyl-9,10-ethanoanthracene. A suspension of 2,3,6,7-tetramethoxy-9,10-dimethylantracene (5 g.) in benzene (300 ml.) was heated at 250° with ethylene at 165 atm. for 3 days with stirring. The resulting solid was collected and crystallised from ethanol, giving the ethanoanthracene (3.4 g.), m. p. 186—186.5° which did not depress the m. p. of the veratrole-hexane-2,5-dione product. The infrared spectra of the two specimens were identical.

Methylation of the catechol-hexane-2,5-dione product. The condensation product prepared by Niederl and Nagel's method⁴ in 46% yield had m. p. 300—301°, λ_{max} 2980 Å (log ϵ 4.04), λ_{inf} 2200 Å (log ϵ 4.29). A solution of the compound (10 g.) in dry acetone (150 ml.) was heated under reflux for 2 hr. with anhydrous potassium carbonate (30 g.) and dimethyl sulphate (30 ml.). After evaporation of the solvent under reduced pressure the remaining solid was washed with water and crystallised from ethanol, giving 9,10-dihydro-2,3,6,7-tetramethoxy-9,10-dimethyl-9,10-ethanoanthracene (10.7 g.), m. p. 185—186°. There was no depression of m. p. on admixture with an authentic specimen, and the infrared spectra of the two preparations were identical.

We are indebted to Drs. A. M. Meston and J. M. C. Thompson for drawing our attention to this problem, and to the Carnegie Trust for the award of a postgraduate scholarship (to I. M. D.).

CHEMISTRY DEPARTMENT, THE UNIVERSITY, OLD ABERDEEN. [Received, November 30th, 1962.]

² Werber, Arcoletto, and Garofano, *Ann. Chim. (Italy)*, 1960, **50**, 1488.

³ Cf. Thomas, U.S.P. 2,406,645/1946.

⁴ Niederl and Nagel, *J. Amer. Chem. Soc.*, 1940, **62**, 3070.

⁵ Le Goff, *Angew. Chem.*, 1962, 407.

⁶ Müller, Raltschewa, and Papp, *Ber.*, 1942, **75**, 692.

585. *Metal-Pyrazine Complexes. Part II.¹ Binuclear Copper(I) Derivatives.*

By A. B. P. LEVER, J. LEWIS, and R. S. NYHOLM.

In an earlier publication² we discussed complexes of the general formula LCu_2X_2 where L is pyrazine or a methylpyrazine and $X = Cl, Br, I, \text{ or } CN$. They are readily prepared by reaction of a stoichiometric quantity of cupric salt with the pyrazine in the presence of hypophosphorous acid; for the cyanides and iodides, the reducing acid is unnecessary. The reducing agent is also unnecessary in the case of tetramethylpyrazine which forms cuprous derivatives when warmed with cupric salts. In this case it is likely that the two *o*-methyl groups hinder the formation of square-planar cupric derivatives and thereby stabilise the linear cuprous complex.³

The pyrazinecopper(I) complexes are yellow or orange solids, insoluble in all solvents except mineral acids (from which they may be recrystallised). On the basis of an empirical infrared correlation¹ we concluded² that there is a copper atom bound to each nitrogen atom of the pyrazine unit (cf. I). An *X*-ray investigation⁴ of the polymeric



dibromo-2,5-dimethylpyrazinenickel^{2,5} has been completed and has confirmed that pyrazines can form bonds at each end to different metal atoms, thus supporting the formulation (I) above.

The complexes are not soluble enough for a molecular-weight determination. This low solubility suggests that they may, in fact, be highly polymeric. However, polymerisation must involve cyanide bridges to three-co-ordinate or tetrahedral four-co-ordinate cuprous atoms; one would then expect, for the cyanide complexes, that the observed infrared-active cyanide stretching vibration would be split, whereas we observe a single frequency (see Table). Moreover, bridging cyanide stretching vibrations are expected to occur at appreciably higher frequencies⁶ than those we observe. We therefore conclude that the cyanide complex is binuclear and infer that the halide complexes are of similar type. The infrared spectra listed in the Table are therefore held to be characteristic of a pyrazine unit bonded at both ends to a metal atom.¹

Pyrazines will only quaternise or protonate at one nitrogen atom,⁷ the second apparently being too feebly basic; hence it is surprising that they will accept two metal atoms. The reaction of pyrazine with boron trichloride gave the complex (II) which is virtually a non-electrolyte in acetone (κ 11 ohm⁻¹ mole⁻¹ cm.⁻¹ in 0.001M-solution). This implies that it is not necessary to invoke back-donation from the metal atom to one nitrogen atom as a means of increasing the donor ability of the other, and indicates that the lone pairs of electrons on both nitrogen atoms are available for the right kind of acceptor atoms.

It is of interest that, with pyrazine itself, the chloride and the bromide complex were not obtained pure, the copper content always being low. Indeed the copper content of these complexes may be reduced simply by washing with water. The cyano- and iodo-pyrazine complexes seem stable. This behaviour is not noted with the methyl-substituted

¹ Lever, Lewis, and Nyholm, *J.*, 1962, 1235.

² Lever, Lewis, and Nyholm, *Nature*, 1961, 189, 58.

³ James and Williams, *J.*, 1961, 2007.

⁴ Ayres, Pauling, and Robertson, personal communication.

⁵ Lever, Lewis, and Nyholm, unpublished work.

⁶ Dows, Haim, and Wilmarth, *J. Inorg. Nuclear Chem.*, 1961, 12, 83.

⁷ Stoehr, *J. prakt. Chem.*, 1893, 47, 439; Brandes and Stoehr, *ibid.*, 1896, 55, 501.

Infrared spectra of pyrazinecopper(I) derivatives, at 2500—650 cm^{-1} (Nujol mulls; CN stretching frequencies in italics).

Dicyano(pyrazine)dication(I) (orange-yellow)	2132s	2119sh	1639w	1409s	1158s	1121s	1096w	1072w	1041s	800s	734m	720m			
Di-iodo(pyrazine)dication(I) (mustard-yellow)	—	—	—	1409s	1153s	1117s	1075vw	1063vw	1047s	800s	734w	720w			
Dichloro(methylpyrazine)dication(I) (orange)	—	1590w	1509m	1397w	1297m	1176sh	1163s	1151s	1074m	1031m	972vw	917vw	833vs	738m	721m
Dicyano(methylpyrazine)dication(I) (yellow)	2103s	1590w	1509m	1397w	1297m	1176m	1165s	1156s	1074s	1031s	966w	—	836s	738m	721m
Dichloro-(2,5-dimethylpyrazine)dication(I) (yellow-orange)	—	—	1484s	1328w	1258vw	1157s	1064s	1031m	962m	884m	746m	719m			
Dibromo-(2,5-dimethylpyrazine)dication(I) (mustard-yellow)	—	—	1484s	1328s	1261w	1156s	1064s	1043s	980m	884s	746w	719w			
Dicyano-(2,5-dimethylpyrazine)dication(I) (yellow)	2103s	1821m	1490s	1389m	1330s	1260m	1164s	1064s	1031m	988m	892m	746m	719m		
Dichloro-(2,6-dimethylpyrazine)dication(I) (orange)	1515m	1399w	1291vw	1263m	1040s	1030s	976w	948m	918w	867s	735s	722m			
Dibromo-(2,6-dimethylpyrazine)dication(I) (orange)	1515m	1399w	1291w	1263m	1170s	1041m	1030m	976m	948m	918w	866s	735s	720s		
Dibromo(tetramethylpyrazine)dication(I) (yellow)	—	1399m	1304w	1253w	1230w	1170s	990s	820s	732sh	719s					
Dicyano(tetramethylpyrazine)dication(I) (yellow)	2130s	1399m	1304sh	1233m	1217m	1172s	980s	807s	732sh	719s					

derivatives and is therefore not likely to be a lattice-energy effect. We conclude tentatively that, in the case of the very weak base pyrazine, the stability of the binuclear complex increases with decreasing electronegativity of the CuX group, since under these conditions the availability of the lone pair of electrons on the second nitrogen atom is at a maximum. In addition, we note⁵ that unstable complexes of the type LCuX can be obtained with pyrazine and mono- and di-methylpyrazine, but not with tetramethylpyrazine which gives only binuclear complexes.

Experimental.—Carbon and hydrogen analyses were carried out in this Department by Mr. A. Winter. Infrared spectra were measured with a Grubb-Parsons GS.2a spectrometer and are given in the Table together with colours.

Dichloro(methylpyrazine)dication(I). Methylpyrazine (1 g., 1 mol.) and cupric chloride dihydrate (3.6 g., 2 mol.) were dissolved in water (100 ml.). 31% Hypophosphorous acid (10 ml.) was added and the mixture kept at 90° for $\frac{1}{2}$ hr. Orange crystals (2.5 g., 55%) were rapidly formed in the hot solution. These were dissolved in the minimum quantity of concentrated hydrochloric acid and filtered through sintered glass. To the acid solution was added cold water, drop by drop, until precipitation was complete. The product was filtered off, washed with water, alcohol, and ether and dried at $60^\circ/15$ mm. (Found: C, 21.2; H, 2.1; N, 10.1; Cu, 44.0; Cl, 24.4. $\text{C}_5\text{H}_8\text{Cl}_2\text{Cu}_2\text{N}_2$ requires C, 20.6; H, 2.1; N, 9.6; Cu, 43.5; Cl, 24.3%).

Dichloro-(2,5-dimethylpyrazine)dication(I) was prepared similarly (Found: Cu, 41.5; Cl, 23.05; N, 9.2. $\text{C}_6\text{H}_8\text{Cl}_2\text{Cu}_2\text{N}_2$ requires Cu, 41.5; Cl, 23.2; N, 9.15%).

Dibromo-(2,5-dimethylpyrazine)dication(I) was also obtained as above but concentrated hydrobromic acid was used for recrystallisation (Found: Br, 40.8; Cu, 32.1; N, 7.0. $\text{C}_6\text{H}_8\text{Br}_2\text{Cu}_2\text{N}_2$ requires Br, 40.5; Cu, 32.2; N, 7.1%).

Dibromo(tetramethylpyrazine)dication(I). Cupric bromide (1 g.) and tetramethylpyrazine (2.4 g.) were refluxed in ethanol (75 ml.) for 6 hr., giving *dibromo(tetramethylpyrazine)dication(I)* as yellow crystals (0.52 g., 27%). These recrystallised from hydrobromic acid. Higher yields of the product may be obtained by the previously quoted procedure (Found: C, 22.7; H, 2.9; Cu, 29.7; N, 6.6. $\text{C}_8\text{H}_{12}\text{Br}_2\text{Cu}_2\text{N}_2$ requires C, 22.7; H, 2.9; Cu, 30.0; N, 6.6%).

Dichloro-(2,6-dimethylpyrazine)dication(I). Cuprous chloride (1 g.) in concentrated hydrochloric acid (10 ml.) was added to 2,6-dimethylpyrazine (2 g.) dissolved in concentrated hydrochloric acid (10 ml.). The intensely red solution was filtered and water was added, drop by

drop, until precipitation ceased. The *dichloro-(2,6-dimethylpyrazine)dicropper*(I), an orange powder (0.7 g., 45%), recrystallised from concentrated hydrochloric acid (Found: C, 23.3; H, 2.9; Cl, 23.0; Cu, 41.7; N, 9.2. $C_6H_8Cl_2Cu_2N_2$ requires C, 23.5; H, 2.6; Cl, 23.2; Cu, 41.5; N, 9.15%).

Dicyano(methylpyrazine)dicropper(I). Methylpyrazine (0.3 g., 1 mol.), potassium cyanide (0.8 g., 4 mol.), and hydroxylamine hydrochloride (1.0 g.) were dissolved in water (10 ml.). A solution of cupric chloride dihydrate (1.1 g., 2 mol.) in water (10 ml.) was added slowly with stirring. The solution was then boiled gently for $\frac{1}{2}$ hour. A green cupric complex was initially formed which, on warming, was rapidly converted into yellow *dicyano(methylpyrazine)dicropper*(I). This product (0.97 g., 70%) was washed with water and dried at 50°/15 mm. (Found: C, 31.5; H, 2.7; Cu, 46.5; N, 20.2. $C_7H_6Cu_2N_4$ requires C, 30.8; H, 2.2; Cu, 46.5; N, 20.5%).

Dicyano-(2,5-dimethylpyrazine)dicropper(I) was similarly prepared (Found: C, 34.1; H, 3.3; Cu, 44.5; N, 19.9. $C_8H_8Cu_2N_4$ requires C, 33.5; H, 2.8; Cu, 44.2; N, 19.5%); so were *dicyano(tetramethylpyrazine)dicropper*(I) (Found: C, 38.2; H, 4.3; Cu, 40.6; N, 18.1. $C_{10}H_{12}Cu_2N_4$ requires C, 38.1; H, 3.8; Cu, 40.3; N, 17.8%), and *dicyano(pyrazine)dicropper*(I) (Found: C, 28.4; H, 1.9; Cu, 49.7; N, 22.0. $C_6H_4Cu_2N_4$ requires C, 27.8; H, 1.55; Cu, 49.0; N, 21.6%).

Di-iodo(pyrazine)dicropper(I). Pyrazine (0.3 g., 1 mol.) and sodium iodide (2.25 g., 4 mol.; in water, 10 ml.) were added to a solution of cupric chloride dihydrate (1.35 g., 2.2 mol.) in water (10 ml.). After $\frac{1}{2}$ hr. the yellow-brown *product* was filtered off, washed with water, alcohol, and ether, and dried at 120°/15 mm. (Found: C, 10.55; H, 1.3; Cu, 27.8; N, 5.7. $C_4H_4Cu_2I_2N_2$ requires C, 10.4; H, 0.9; Cu, 27.6; N, 6.1%).

Pyrazine-boron trichloride adduct. Boron trichloride (2 mol.), dissolved in chloroform (10 ml.), was added drop by drop to pyrazine (1 mol.), also in chloroform (10 ml.). The white *product* was washed with chloroform and dried in a desiccator (Found: C, 15.0; H, 1.5; Cl, 67.6. $C_4H_4B_2Cl_6N_2$ requires C, 15.2; H, 1.3; Cl, 67.6%).

We are grateful to the Wyandotte Chemical Corp., Michigan, U.S.A. for financial assistance and for the supply of pyrazines.

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586. Hydrolysis of N-Alkyl-N-nitrosoaspartic Anhydrides.

By F. H. C. STEWART.

RECENTLY¹ it was found that *N*-2'-cyanoethyl-*N*-nitroso-*L*-glutamic anhydride (I) reacted with water at room temperature to give 3-2'-cyanoethyl-4-2'-carboxyethylsydnone (II) in 35% yield in addition to the expected nitrosoglutamic acid. This anhydride, however, showed no tendency to isomerise to the sydnone (II) on storage, or when heated in an inert solvent, contrary to what might have been expected for a mixed anhydride derived from an *N*-alkyl-*N*-nitroso- α -amino-acid.² This unusual mode of sydnone formation may be a result of participation of the *N*-nitroso-group in the hydrolysis of the anhydride ring, possibly involving the mesomeric bicyclic cation (III), so it was of interest to investigate the behaviour of two readily available five-membered analogues of the anhydride (I) under similar conditions.

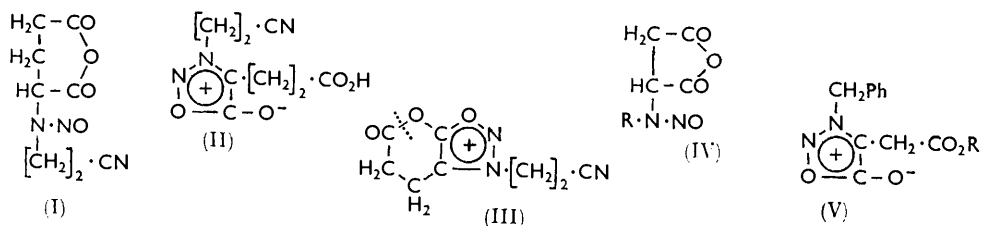
Brookes and Walker³ obtained *N*-benzyl-*N*-nitroso-*DL*-aspartic anhydride (IV; R = CH₂Ph) by the action of acetic anhydride on the corresponding nitroso-acid. The isomeric sydnone (V; R = H) was not produced, and the anhydride was not converted into it under the usual conditions. Hydrolysis of this anhydride by water has now been examined and the products analysed spectroscopically. With aqueous acetone at room

¹ Stewart, *J.*, 1963, 701.

² Baker, Ollis, and Poole, *J.*, 1950, 1542.

³ Brookes and Walker, *J.*, 1957, 4409.

temperature it gave predominantly *N*-benzyl-*N*-nitroso-DL-aspartic acid, but 3-benzyl-4-carboxymethylsydnone (V; R = H) was also formed in 3–4% yield. When the anhydride was boiled briefly with water, the yield of sydnone was increased to ~30%. *N*-2'-Cyanoethyl-*N*-nitroso-L-aspartic anhydride (IV; R = [CH₂]₂·CN), prepared by the action of acetic anhydride on *N*-2'-cyanoethyl-*N*-nitroso-L-aspartic acid, reacted similarly



with water at room temperature to give a mixture containing 2–5% of a sydnone. Comparison of the optical rotation of the product with that of the parent acid indicated considerable racemisation during hydrolysis.

These results suggest that sydnone formation is less favoured in the hydrolysis of the five-membered cyclic anhydrides than in that of the glutamic analogue (I). This may be due to the increased strain imposed by fusion of the smaller ring to the planar mesomeric nucleus of an intermediate such as (III).

3-Benzyl-4-carboxymethylsydnone (V; R = H) was synthesised for reference as follows. β -Methyl hydrogen *N*-benzyl-DL-aspartate was prepared by addition of benzylamine to methyl hydrogen maleate.⁴ Treatment of the derived *N*-nitroso-derivative with acetic anhydride gave 3-benzyl-4-carboxymethylsydnone (V; R = Me), which was selectively hydrolysed, without cleavage of the sydnone ring, in boiling water in the presence of a strong-acid exchange resin.

Experimental.—*Hydrolysis of N-benzyl-N-nitroso-DL-aspartic anhydride* (IV; R = CH₂Ph). (a) The anhydride³ (100 mg.) was boiled with water whereupon it rapidly dissolved. The cooled solution was saturated with sodium chloride and extracted with ethyl acetate. Evaporation of the dried extract gave a residue which, when washed with light petroleum (yield 94 mg.), had m. p. 115–119°. The product gave a strong Liebermann reaction. The infrared spectrum (in KBr) was compared with those of *N*-benzyl-*N*-nitroso-DL-aspartic acid and 3-benzyl-4-carboxymethylsydnone (V; R = H). The intensity of the ultraviolet maximum at 300 m μ indicated that ~30% of the sydnone was present. The absorption due to the nitroso-acid occurred at 238 m μ .³

(b) A solution of the anhydride (100 mg.) in acetone (3.0 ml.) was treated with water (5.0 ml.) at room temperature for 2 hr., the acetone removed *in vacuo*, and the residue worked up as in (a). The solid product (85 mg., m. p. 134–137°) contained 3–4% of the sydnone (V; R = H), estimated as before.

N-Benzyl-*N*-nitroso-DL-aspartic acid, prepared as described by Brookes and Walker,³ had m. p. 140.5–141.5°.

N-2'-Cyanoethyl-L-aspartic acid. L-Aspartic acid was cyanoethylated as described for the DL-isomer.⁵ The acid, m. p. 182–184° (decomp.), $[\alpha]_D^{26}$ 21.5° (*c* 2 in 3*N*-HCl), recrystallised from aqueous ethanol (Found: C, 45.3; H, 5.3; N, 14.5. C₇H₁₀N₂O₄ requires C, 45.2; H, 5.4; N, 15.1%).

N-2'-Cyanoethyl-*N*-nitroso-L-aspartic anhydride (IV; R = [CH₂]₂·CN). An ice-cold solution of *N*-2'-cyanoethyl-L-aspartic acid (2.0 g.) and concentrated hydrochloric acid (1.0 ml.) in water (3.0 ml.) was treated with an aqueous solution of sodium nitrite (0.8 g.). After 30 min. urea was added and the solution extracted with ethyl acetate. Evaporation of the dried extract

⁴ Cf. Laliberté and Berlinguet, *Canad. J. Chem.*, 1962, **40**, 163.

⁵ McKinney, Uhing, Setzkorn, and Cowan, *J. Amer. Chem. Soc.*, 1950, **72**, 2599.

gave the nitroso-derivative as a yellow oil, $[\alpha]_D^{24} - 73.7^\circ$ (*c* 4 in ethyl acetate). This was treated with acetic anhydride (8.0 ml.) at room temperature. After 12 hr. the mixture was diluted with ether, and the *anhydride* (IV; R = $[\text{CH}_2]_2\text{CN}$) collected (1.75 g., 89%); it had m. p. 137—139° (decomp.), ν_{max} (in KBr) 2260 (CN), 1880, 1800 (CO·O·CO), 1410 cm^{-1} (NO), $[\alpha]_D^{27} - 26.1^\circ$ (*c* 1 in ethyl acetate). Recrystallised from ethyl acetate–light petroleum, it had m. p. 141—142° (decomp.) (Found: C, 42.6; H, 3.7; N, 21.5. $\text{C}_7\text{H}_7\text{N}_3\text{O}_4$ requires C, 42.6; H, 3.5; N, 21.3%).

Hydrolysis of N-2'-cyanoethyl-N-nitroso-L-aspartic anhydride. The anhydride (200 mg.) was treated with an excess of water at room temperature for 2—3 hr., and the solution was saturated with sodium chloride and extracted with ethyl acetate. Evaporation of the dried extract gave an oil, $[\alpha]_D^{24.5} - 35.2^\circ$ (*c* 4 in ethyl acetate). The ultraviolet spectrum showed a peak at 298 $\text{m}\mu$ with an intensity corresponding to 2—5% of a sydnone.² Treatment of the crude hydrolysis product with acetic anhydride gave the parent anhydride (IV; R = $[\text{CH}_2]_2\text{CN}$) in 83% overall recovery.

β -Methyl hydrogen N-benzyl-DL-aspartate. Methyl hydrogen maleate was treated with benzylamine and triethylamine by the procedure of Laliberté and Berlinguet;⁴ the required *ester* was obtained in 56% yield, forming leaflets (from aqueous methanol), m. p. 212—213° (decomp.) (Found: C, 60.8; H, 6.4; N, 6.0. $\text{C}_{12}\text{H}_{15}\text{NO}_4$ requires C, 60.8; H, 6.3; N, 5.9%).

3-Benzyl-4-carbomethoxymethylsydnone (V; R = Me). A suspension of β -methyl hydrogen *N*-benzyl-DL-aspartate (9.0 g.) in water (30 ml.) was treated with concentrated hydrochloric acid (3.4 ml.). The hydrochloride separated. An aqueous solution of sodium nitrite (2.9 g.) was added in portions to the ice-cooled mixture with shaking. A semi-solid mass was formed which was extracted with warm ethyl acetate. The dried extract was evaporated *in vacuo*, leaving an oily *N*-nitroso-derivative which was treated with acetic anhydride (30 ml.) for 3 days at room temperature. The mixture was hydrolysed by warm water (10 ml.), then diluted and extracted with chloroform. The extract was washed with sodium hydrogen carbonate solution and dried (Na_2SO_4). Evaporation left the *sydnone* (5.2 g., 56% overall), m. p. 89—91°. It formed needles (from ethyl acetate–light petroleum), m. p. 91—92°, ν_{max} (in KBr) 1745 (sydnone CO), 1735 cm^{-1} (ester CO), λ_{max} (in MeOH) 297 $\text{m}\mu$ (ϵ 5000) (Found: C, 57.9; H, 4.8; N, 11.3. $\text{C}_{12}\text{H}_{13}\text{N}_2\text{O}_4$ requires C, 58.1; H, 4.8; N, 11.3%).

3-Benzyl-4-carboxymethylsydnone (V; R = H). 3-Benzyl-4-carbomethoxysydnone (300 mg.) and Dowex 50 resin (900 mg.) in the hydrogen form were refluxed in water (5 ml.) for 1 hr. The solution was filtered while hot and the filtrate extracted with chloroform. Evaporation of the dried extract gave the *sydnone* (117 mg.) which was washed with ether and formed needles (from ethyl acetate–light petroleum), m. p. 132.5—133.5°, ν_{max} (in KBr) 1740 (sydnone CO), 1690 cm^{-1} (CO_2H), λ_{max} (in MeOH) 301 $\text{m}\mu$ (ϵ 6400) (Found: C, 56.5; H, 4.4; N, 12.2. $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}_4$ requires C, 56.4; H, 4.3; N, 12.0%).

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587. Bent Bonds in Cycloalkanes: a Correction.

By C. A. COULSON and T. H. GOODWIN.

IN our paper¹ on the bent bonds in cycloalkanes we applied the principle of maximum overlap to determine the form of the atomic orbitals at the carbon atoms of the compounds $[\text{CH}_2]_n$ when $n = 3, 4$, or 5 , all the carbon atoms being treated as coplanar. Assuming lengths of 1.53 and 1.07 \AA for the C-C and C-H bonds we used and quoted various overlap integrals taken from Sahni and Cooley's tables.² Dr. H. Looyenga, of the Centraal Laboratorium T.N.O., Delft, Holland, has recently written to us that the values of the integrals I_5 and I_6 which we quoted do not agree with those derived from other tables and sources and we now find that we were in error, having taken our figure for I_5 from the tables $S(1s, 2s)$ instead of from $S(2s, 1s)$ and that for I_6 from $S(1s, \sigma, 2p)$ instead of from $S(2p, \sigma, 1s)$; two tables are given in each case to avoid including values for negative τ (one to the tabulation parameters). The correct values of these integrals are $I_5 = 0.5809$ and $I_6 = 0.4699$.

These lead to the annexed revision of the Table in our paper. These revised figures are generally more satisfactory than the earlier ones. In particular ω for cyclopropane differs from the value of 22° obtained by Coulson and Moffitt,³ by only half a degree, thus showing that the result of this relatively simple calculation is remarkably close to the

	$n = 3$	$n = 4$	$n = 5$		$n = 3$	$n = 4$	$n = 5$
a	0.4266	0.4502	0.4640	λ_{1H}	1.4645	1.5372	1.5851
b	0.5639	0.5453	0.5336	ξ_{1H}	$31^\circ 06'$	$32^\circ 29'$	$33^\circ 16'$
λ_{12}	2.1199	1.9834	1.9090	$\pi - 2\xi_{1H}$	$117^\circ 48'$	$115^\circ 02'$	$113^\circ 28'$
ξ_{12}	$38^\circ 34'$	$37^\circ 38'$	$37^\circ 02'$	S_{max}	6.0410	8.1842	10.2523
ω_{12}	$21^\circ 26'$	$7^\circ 22'$	$-1^\circ 02'$	S_{tet}	6.0011	8.1593	10.2362
$\pi - 2\xi_{12}$	$102^\circ 52'$	$104^\circ 44'$	$105^\circ 56'$				

more elaborate and probably more accurate one. For cyclopentane, a positive value of ω of about $0^\circ 20'$ was expected; the negative value of $1^\circ 02'$ is therefore rather surprising, though probably not significant but attributable either to the somewhat arbitrary selection of C-C and C-H bond lengths or to the fundamental approximation of the criterion of maximum overlap. As was anticipated before the earlier calculations the angle $\pi - 2\xi_{12}$ between the axes of the orbitals forming the C-C bonds is appreciably, though not enormously, less than the tetrahedral angle but increases towards this as n increases to 5. This is much more satisfactory than the earlier result which suggested that this angle increased beyond the tetrahedral for $n = 4$ and $n = 5$. Yet again the H-C-H angles of $117^\circ 48'$ and $115^\circ 02'$ now obtained for cyclopropane and cyclobutane agree considerably better with the experimental values of $113.6^\circ \pm 2^\circ$ ⁴ and $114^\circ \pm 8^\circ$;⁵ no measurement has been made for cyclopentane.

We take advantage of this note to point out the omission of b after the $\sqrt{2}$ in the coefficients multiplying I_3 and I_4 in the expression for S on p. 2853 and that, three lines further on, $\pi - 2\xi$ should be defined as the angle between the axes of ψ_{12} and ψ_{1n} .

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¹ Coulson and Goodwin, *J.*, 1962, 2851.

² Sahni and Cooley, "Derivation and Tabulation of Molecular Integrals," New York Univ. and National Aeronautics and Space Administration, Washington, Technical Note D-146-I.

³ Coulson and Moffitt, *Phil. Mag.*, 1949, 40, 1.

⁴ Bastiansen and Skancke, *Adv. Chem. Phys.*, 1960, 3, 323.

⁵ Dunitz and Schomaker, *J. Chem. Phys.*, 1952, 20, 1705.

588. *A New Synthesis of Flavans.*

By E. J. KEOGH, EVA M. PHILBIN, S. USHIODA, and (the late)
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REDUCTIVE desulphurisation of ethylene dithioketals of certain flavanones gives the corresponding flavans in satisfactory yield.¹ The method is of value in the preparation of catechin derivatives. Quercetin (5,7,3',4'-tetrahydroxyflavonol) was reduced by sodium dithionite to the corresponding dihydroflavonol,² which on methylation afforded the 5,7,3',4'-tetramethyl ether.³ The last compound was converted through the ethylene dithioketal into (\pm)-catechin 5,7,3',4'-tetramethyl ether. When this series of reactions was applied to the 3-*O*-acetyl derivative of dihydroquercetin 5,7,3',4'-tetramethyl ether, the 3-acetates of both (\pm)-catechin tetramethyl ether and 5,7,3',4'-tetramethoxyflavan were obtained. The formation of a catechin, and not an epicatechin, derivative from quercetin corroborates the finding of Clark-Lewis and Korytnyk⁴ that the reduction by sodium dithionite involves 2,3-*trans*-addition of hydrogen. An attempt to synthesise an afzelechin⁵ (3,5,7,4'-tetrahydroxyflavan) derivative from 3,4'-dihydroxy-5,7-dimethoxyflavanone⁶ was not successful.

Experimental.—Flavanones. The following flavanones were prepared: flavanone;⁷ 4'-methoxyflavanone;⁸ 3-hydroxyflavanone (dihydroflavonol);⁹ 3-acetoxyflavanone;¹⁰ 3-benzoyloxyflavanone¹¹ (Found: C, 77.0; H, 4.9. Calc. for C₂₂H₁₆O₄: C, 76.7; H, 4.7%), m. p. 156—158° (plates from ethanol); 3-hydroxy-5,7,3',4'-tetramethoxyflavanone (dihydro-5,7,3',4'-tetramethoxyflavonol);³ and 3-acetoxy-5,7,3',4'-tetramethoxyflavanone.⁴

Ethylene dithioketals. A mixture of flavanone (0.25 g.), 1,2-ethanedithiol¹² (0.3 ml.), and boron trifluoride-ether complex (0.3 ml.) was kept for 3 hr. at room temperature and then treated with aqueous sodium carbonate until alkaline. The mixture yielded, to ether, *flavanone ethylene dithioketal* (0.25 g.), m. p. 120—121° (prisms from benzene-ligroin) (Found: C, 68.4; H, 5.5; S, 21.2. C₁₇H₁₆OS₂ requires C, 68.0; H, 5.4; S, 21.3%).

The following thioketals were similarly prepared: 4'-*Methoxyflavanone ethylene dithioketal*, m. p. 132° (from ligroin) (Found: C, 65.6; H, 5.6; S, 18.8. C₁₈H₁₈O₂S₂ requires C, 65.4; H, 5.5; S, 19.4%); *dihydroflavonol ethylene dithioketal*, m. p. 154—156° (from benzene-ligroin) (Found: C, 64.1; H, 5.2; S, 19.7. C₁₇H₁₆O₂S₂ requires C, 64.6; H, 5.1; S, 20.2%); 3-*acetoxyflavanone ethylene dithioketal*, m. p. 152—153° (plates from methanol) (Found: C, 63.8; H, 5.3; S, 17.5. C₁₉H₁₈O₃S₂ requires C, 63.7; H, 5.1; S, 17.9%); 3-*benzoyloxyflavanone ethylene dithioketal*, m. p. 163—164° (prisms from ethanol) (Found: C, 69.1; H, 4.8; S, 14.8. C₂₄H₂₀O₃S₂ requires C, 68.6; H, 4.8; S, 15.2%); 3-*hydroxy-5,7,3',4'-tetramethoxyflavanone ethylene dithioketal* (A), m. p. 175—177° (prisms from ethanol) (Found: C, 58.0; H, 5.6; S, 14.3; OMe, 28.9. C₂₁H₂₄O₆S₂ requires C, 57.8; H, 5.5; S, 14.7; 4OMe, 28.4%); 3-*acetoxy-5,7,3',4'-tetramethoxyflavanone ethylene dithioketal* (B), m. p. 153—154° (prisms from methanol) (Found: C, 57.4; H, 5.5; S, 13.7. C₂₃H₂₆O₇S₂ requires C, 57.7; H, 5.5; S, 13.4%).

Desulphurisation of thioketals. Flavanone ethylene dithioketal (1 g.) was refluxed with Raney nickel (10 g.) in dioxan (150 ml.) for 8 hr. Removal of the catalyst and solvent at reduced pressure gave an oil which after purification on an alumina column formed crystals (0.5 g.), m. p. and mixed m. p. with an authentic sample of flavan,¹³ 44—45°.

¹ Keogh, Philbin, Ushioda, and Wheeler, *Chem. and Ind.*, 1961, 2100.

² Geissman and Lischner, *J. Amer. Chem. Soc.*, 1952, **74**, 3001.

³ Hergert, Coad, and Logan, *J. Org. Chem.*, 1956, **21**, 304.

⁴ Clark-Lewis and Korytnyk, *J.*, 1953, 2367.

⁵ King, Clark-Lewis, and Forbes, *J.*, 1955, 2948.

⁶ Guider, Simpson, and Thomas, *J.*, 1955, 170.

⁷ Löwenbein, *Ber.*, 1924, **57**, 1515.

⁸ Karrer, Yen, and Reichstein, *Helv. Chim. Acta*, 1930, **13**, 1308.

⁹ Reichel and Steudel, *Annalen*, 1942, **553**, 83.

¹⁰ Cavill, Dean, McGookin, Marshall, and Robertson, *J.*, 1954, 4573.

¹¹ Fletcher, Ph.D. Thesis (N.U.I.), 1958, p. 195.

¹² Speziale, *Org. Synth.*, 1950, **30**, 35.

¹³ Hultzsich, *J. prakt. Chem.*, 1941, **158**, 275.

The following flavans were prepared from their thioketals mentioned above: 4'-methoxyflavan, b. p. 160—162°/3 mm., m. p. 82° (lit.,¹⁴ 83—84°) (Found: C, 79.7; H, 6.5. Calc. for C₁₆H₁₆O₂: C, 80.0; H, 6.7%). 3-hydroxy-5,7,3',4'-tetramethoxyflavan [(±)-catechin 5,7,3',4'-tetramethyl ether], m. p. 145—146° (lit.,¹⁵ 142°) [acetate, m. p. 134—135° (see below) (lit.,⁴ 135—136°) (Found: C, 64.8; H, 6.1; OMe, 32.2. Calc. for C₂₁H₂₄O₇: C, 64.9; H, 6.2; 4OMe, 31.9%)]. The product from the desulphurisation of thioketal (B) (see above) was separated by fractional crystallisation from methanol into two products: (i) 3-acetoxy-5,7,3',4'-tetramethoxyflavan,⁴ m. p. 134—135°, not depressed on admixture with the acetate, m. p. 134—135°, obtained through the thioketal (A) (see above); and (ii) 5,7,3',4'-tetramethoxyflavan, m. p. 110—111° (lit.,¹⁶ 111°) (Found: C, 69.4; H, 6.8; OMe, 36.9. Calc. for C₁₉H₂₂O₅: C, 69.1; H, 6.7; 4OMe, 37.7%). The *α*-bromo-product had m. p. 155—156° (lit.,¹⁶ 155—156°).

The third, fourth, and fifth thioketal mentioned above gave no useful result on treatment with Raney nickel.

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¹⁴ Brown and Cummings, *J.*, 1958, 4302.

¹⁵ Freudenberg and Purtmann, *Annalen*, 1924, 437, 274.

¹⁶ Freudenberg and Kammüller, *Annalen*, 1927, 451, 209.

589. Uranium(IV) Chloride Complexes of 1,2-Dimethylthioethane, 1,2-Dimethoxyethane, and Tetra-P-methylethylenediphosphine.

By H. C. E. MANNERSKANTZ, G. W. PARSHALL, and G. WILKINSON.

FEW complexes of uranium tetrachloride with π -bonding ligands have been reported,¹ the best known being the alkylphosphine derivatives (R₃P)₂UCl₄ where R = Et or Pr,² and, although no donor sulphur complexes appear to have been isolated, uranium tetrachloride is reported to be soluble in dimethyl sulphide.³ We have added two further examples.

Experimental.—Reaction of uranium tetrachloride (1.2 g., 3.17 mmoles) in dry tetrahydrofuran (50 ml.) with 1,2-dimethylthioethane (0.53 ml., 6.34 mmoles) under nitrogen at room temperature for 24 hr. gave, after removal of solvent *in vacuo*, an essentially quantitative yield of a grey-green complex, UCl₄L₂, which was washed several times with light petroleum under nitrogen (Found: C, 15.3; H, 3.5; Cl, 22.1; U, 37.9. C₈H₂₀Cl₄S₄U requires C, 15.4; H, 3.2; Cl, 22.7; U, 38.2%). The compound, which is sensitive to air, can be kept under nitrogen for several months. In a closed tube it decomposes at 150°. It is insoluble in benzene but is soluble in tetrahydrofuran and in nitrobenzene; in the latter it is essentially non-conducting. The infrared spectrum has bands at 2390w, 1595w, 1463sh, 1450sh, 1420m, 1370sh, 1313w, 1295sh, 1282w, 1265w, 1028w, 1015w, 971w, 913w, and 840w cm.⁻¹ (Nujol and hexachlorobutadiene mulls, NaCl optics). By comparison with the spectra of 1,2-dimethylthioethane⁴ and other complexes of this ligand⁵ it can be concluded that the sulphur ligand occurs in its gauche form in the uranium complex, which is thus most probably 8-co-ordinate, although this is not completely certain since its molecular weight could not be obtained by either the ebullioscopic method in benzene or the isopiestic method in tetrahydrofuran.

The oxygen analogue can be prepared from 1,2-dimethoxyethane ("Dimethylcellosolve").

¹ Comyns, *Chem. Rev.*, 1960, 60, 128.

² Allison and Mann, *J.*, 1949, 2915.

³ "Dimethyl Sulphide, an Organic Solvent for Inorganic Compounds," Crown Zellerbach Corp., Damas, Washington, U.S.A.

⁴ Sweeney, Mizushima, and Quagliano, *J. Amer. Chem. Soc.*, 1955, 77, 6521.

⁵ Mannerskantz and Wilkinson, *J.*, 1962, 4454.

If uranium tetrachloride (1.4 g.) and the ether (distilled *in vacuo*) (9 g.) are set aside for 24 hr. at room temperature, the dark green uranium tetrachloride dissolves and a pale green solid separates. Removal of solvent *in vacuo* leaves grey-green crystals (2 g., *ca.* 96%) of a *complex*, UCl_4L_2 , which has an infrared spectrum almost identical with that of the ether except that the bands at 1245 and 1107 cm^{-1} in the latter are shifted to 1263 and 1080 cm^{-1} , respectively, and two new bands appear at 801 and 832 cm^{-1} (Found: C, 17.3; H, 3.3; Cl, 25.4. $\text{C}_8\text{H}_{20}\text{Cl}_4\text{O}_4\text{U}$ requires C, 17.1; H, 3.6; Cl, 25.3%).

3,6,9-Trithiaundecane and uranium tetrachloride react, as is shown by a colour change and formation of a grey-green solid; the latter was very sensitive to air and gave unsatisfactory analyses.

Attempts to prepare an analogous bidentate phosphine complex led to the formation of a highly insoluble compound which had only one diphosphine molecule attached to uranium tetrachloride; it is presumably an octahedral complex. A solution of uranium tetrachloride (7.6 g., 20 mmoles) in ethanol (35 ml.) was treated with tetra-*P*-methylethylenediphosphine (7.5 g., 50 mmoles). The light-tan solid *complex*, UCl_4L , which separated was washed with ethanol and with ether and was dried under reduced pressure (Found: C, 13.1; H, 3.5; P, 10.3. $\text{C}_6\text{H}_{16}\text{Cl}_4\text{P}_2\text{U}$ requires C, 13.6; H, 3.0; P, 11.7%).

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