740. *The Reaction of Copper with Suspensions of Nitrosyl Perchlorate.*

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Nitrosyl perchlorate reacts with copper, when suspended in certain organic solvents, according to the equation: $Cu + 2NO^+ClO_4^- = Cu(ClO_4)_2 + 2NO$. If the reaction is carried out at atmospheric pressure, the solution of copper perchlorate is contaminated with copper nitate, but under reduced pressure a solution of the pure perchlorate is obtained. Some physical properties (molecular weight, electrical conductivity, visible and ultraviolet spectra) of the solutions of copper perchlorate have been examined and the nature of the solid phases which have been separated from the concentrated solutions is discussed.

THE existence of the nitrosyl ion NO^+ has been clearly established in a number of crystalline compounds, such as nitrosyl perchlorate and tetrafluoroborate, and its general properties have been determined from these compounds.[1,2] Little is known, however, of the reactions of the nitrosyl ion in which it acts as an oxidising agent and is itself reduced to nitric oxide:

$$NO^+ + e \longrightarrow NO \qquad (1)$$

Seel [3] has shown that this occurs when sodium metal reacts with nitrosyl hexachloroantimonate(V) in liquid sulphur dioxide:

$$Na + NO^+SbCl^-_6 \longrightarrow NaSbCl_6 + NO \qquad (2)$$

Addison, Sheldon, and Hodge [4] have shown that dinitrogen tetroxide behaves as nitrosyl nitrate in organic donor solvents and will react with copper, zinc, and uranium with evolution of nitric oxide and formation of the metal nitrate:

$$N_2O_4 + n(Don) \longrightarrow (Don)_nNO^+ + NO_3^- \qquad (3)$$

$$Cu + 2(Don)_nNO^+ \longrightarrow Cu^{2+} + n(Don) + 2NO \qquad (4)$$

In general, a nitrosyl compound should react with a metal according to the scheme:

$$nNO^+X^- + M \longrightarrow M(X)_n + nNO \qquad (5)$$

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[1] Angus and Leckie, *Trans. Faraday Soc.*, 1935, **31**, 958.
[2] Klinkenberg, *Rec. Trav. chim.*, 1937, **56**, 749.
[3] Seel, *Z. anorg. Chem.*, 1950, **261**, 75.
[4] Addison, Sheldon, and Hodge, *J.*, 1956, 3900.

with formation of a solution of the metal salt, provided a suitable solvent for the reaction can be found. If nitrosyl perchlorate is used then a solution of the anhydrous metal perchlorate should be obtained. In view of the unusual properties of anhydrous copper perchlorate [5] the reaction has been studied by using copper metal.

RESULTS AND DISCUSSION

Solubility of Nitrosyl Perchlorate.—A wide range of anhydrous organic liquids were examined but none was found capable of dissolving nitrosyl perchlorate. A number of organic solvents reacted directly with it, *e.g.*, acetone, diethyl ether, and pyridine; and suspensions of nitrosyl perchlorate in many other solvents were quite stable, *e.g.*, ethyl acetate, methyl cyanide, nitromethane, benzene, n-hexane, and carbon tetrachloride. Nitrosyl perchlorate is also insoluble and inert in a number of inorganic liquids, *e.g.*, phosphorus oxychloride, anhydrous perchloric acid, and dinitrogen tetroxide.

Reaction of Copper with Suspensions of Nitrosyl Perchlorate.—In spite of this insolubility, nitrosyl perchlorate suspended in ethyl acetate, methyl cyanide, or nitromethane reacted with copper, as shown by evolution of nitric oxide from the surface of the metal and development of a green colour throughout the bulk of the liquid. If the suspension of nitrosyl perchlorate was allowed to settle the reaction only occurred at the copper–nitrosyl perchlorate–organic solvent interface and not at the surface which was only immersed in the liquid. This reaction only at the interface suggests that at this interface nitrosyl perchlorate does go into solution, as no reaction occurs in the absence of an organic solvent. Further evidence that solution does occur at this interface is obtained from the observation that reaction will only occur in the presence of an 'onium donor solvent,[6] *i.e.*, a solvent which can co-ordinate to the nitrosyl ion and stabilise it in solution; thus no reaction will occur in benzene (a π-donor), carbon tetrachloride, or n-hexane.

If reaction was at atmospheric pressure, analysis showed the resulting solution to contain cupric, perchlorate, and nitrate ions; if it was carried out under reduced pressure the nitrate content was reduced to less than 1% and a solution of anhydrous copper perchlorate in the organic solvent was obtained. The presence of nitrate in these solutions was unexpected but arises from further reaction of the nitric oxide evolved in the initial reaction: the nitrogen dioxide produced by atmospheric oxidation dimerises in the organic solvent to dinitrogen tetroxide, which then reacts with copper metal according to equations (3) and (4) to give some copper nitrate in solution. In the reaction under reduced pressure the nitric oxide was removed from the reaction mixture before oxidation could occur, thus preventing the formation of any nitrate in the final solution.

When ethyl acetate was used as the organic solvent a steady reaction was obtained under reduced pressure; after its completion the solution was filtered, and a stable, clear, emerald-green filtrate obtained. In methyl cyanide a much faster reaction was obtained, and, as it neared completion, blue crystals were deposited from the solution; these were copper perchlorate solvated by four molecules of methyl cyanide. Filtration at the completion of reaction yielded a stable, clear, blue-green solution. The faster rate of reaction in methyl cyanide is attributed to the higher dielectric constant, *viz.*, 37·5 (compared to 6·02 for ethyl acetate), which would enhance the solubility of the nitrosyl perchlorate at the interface. In addition, the stronger donor properties of methyl cyanide will stabilise the nitrosyl ion in solution and result in a higher concentration of this ion at the interface and lead to faster reactions.

Properties of the Copper Perchlorate Solutions.—Solutions of copper perchlorate in ethyl acetate and methyl cyanide were perfectly stable if kept in a closed tube, but if access of moisture occurred the solution became turbid, and ultimately a gelatinous basic copper perchlorate was precipitated. Evaporation of the solution of copper perchlorate in ethyl

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[5] Hathaway, *Proc. Chem. Soc.*, 1958, 344.

[6] Addison and Sheldon, *J.*, 1956, 1941.

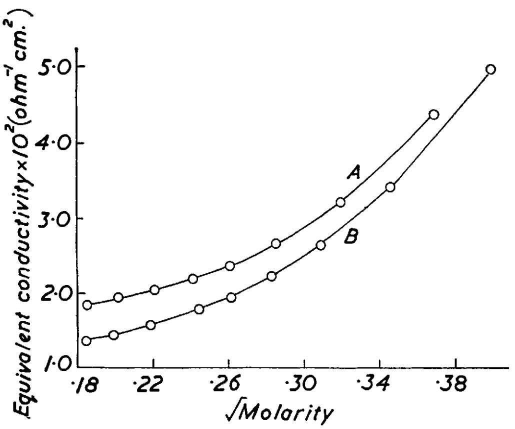
acetate yielded a very viscous emerald-green oil which was very difficult to crystallise. If the oil was stored for 2—3 days it solidified to a pale green crystalline material, shown by analysis to be $Cu(ClO_4)_2,2{\cdot}5EtOAc$. Evaporation of the solution of copper perchlorate in methyl cyanide afforded blue crystals of copper perchlorate tetra(methyl cyanide).

Apparent Molecular Weight of Copper Perchlorate in Solution.—Cryoscopic determinations of the molecular weight in ethyl acetate and methyl cyanide gave the following results:

	Ethyl acetate		Methyl cyanide		
Molarity	0·2043	0·2285	0·1982	0·135	0·0991
Molecular weight	258	258	175	146	131

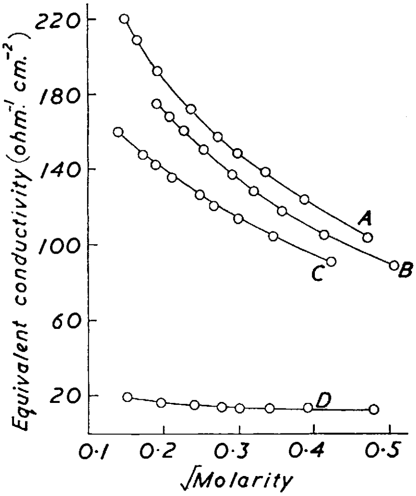
These show that copper perchlorate (*M*, 262·5) is monomeric in boiling ethyl acetate solution, but that in boiling methyl cyanide solution some dissociation occurs which is dependent upon the concentration:

FIG. 1. *Equivalent conductivities of copper perchlorate and copper nitrate in ethyl acetate solution.*



(*A*) $Cu(ClO_4)_2$. (*B*) $Cu(NO_3)_2$.

FIG. 2. *Equivalent conductivities of copper perchlorate and copper nitrate in methyl cyanide solution.*



(*A*) $Cu(ClO_4)_2$ prepared in solution.
(*B*) Sublimed $Cu(ClO_4)_2$.
(*C*) $NEt_4^+ClO_4^-$.
(*D*) Sublimed $Cu(NO_3)_2$.

$$Cu(ClO_4)_2 \rightleftharpoons Cu(ClO_4)^+ + ClO_4^- \rightleftharpoons Cu^{2+} + 2ClO_4^- \quad . \; . \; . \; . \; . \quad (6)$$

On the other hand, anhydrous copper nitrate is monomeric in both these solvents at the above concentrations.[7] Dissociation of copper perchlorate in methyl cyanide is consistent with the higher dielectric constant of this solvent which would enhance dissociation into ionic species. It is also consistent with the much weaker associating properties of the perchlorate ion than of the nitrate ion for metal cations, and therefore the perchlorate would be expected to be more dissociated than the nitrate in an ionising solvent.

Electrical Conductivity of Copper Perchlorate Solutions.—The variation of the equivalent conductivity of copper perchlorate with concentration is shown in Fig. 1 (ethyl acetate) and Fig. 2 (methyl cyanide); in both cases the corresponding values for sublimed copper nitrate in the respective solvents are shown for comparison.[7] The results in ethyl acetate for both the perchlorate and the nitrate are very similar and of very low order (10^{-2} ohm^{-1}

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[7] Addison and Hathaway, in the press.

cm.^{2}), indicating that the solutions are virtually non-conducting. This is consistent with the molecular-weight results, which showed that both compounds are unimolecular in this solvent even at its boiling point. The slightly higher conductivities of the perchlorate than of the nitrate are consistent with the weaker associating power of the perchlorate ion which has resulted in very slight ionisation of the perchlorate even in a solvent with as low a dielectric constant as ethyl acetate (6·02). Why the conductivities increase with increasing concentration is uncertain but it is qualitatively consistent with ion-pair formation.[8]

The equivalent conductivities of copper perchlorate (and copper nitrate for comparison [7]) in methyl cyanide (Fig. 2) are radically different from the values in ethyl acetate. First, they are of a much higher order, 10^2 compared with 10^{-2}; secondly, they decrease with increasing concentration; and thirdly, the equivalent conductivity of the perchlorate is an order of ten higher than that of the nitrate. Clearly, the much higher dielectric constant of methyl cyanide (37·5) than of ethyl acetate (6·02) increases both the dissociation of the salts and the equivalent conductivities. With copper perchlorate the molecular conductivities cover the range 100—200 ohm^{-1} cm.^{2} which is higher than that of tetraethylammonium perchlorate in this solvent (Fig. 2). This indicates extensive ionisation of copper perchlorate in this solvent, a conclusion supported by the apparent molecular weight results previously described. A consequence of this ionisation in methyl cyanide is that the molecular conductivity now decreases with increasing concentration, *i.e.*, a normal Onsager-type equation is obeyed, although the plot of Λ against $\sqrt{c}$ is not linear. The difference between the molecular conductivities of the perchlorate and the nitrate was unexpected, but to check these results the molecular conductivity of sublimed copper perchlorate in methyl cyanide was measured; the results (Fig. 2) lie only slightly below those obtained as above and clearly establish that copper perchlorate is a much better conductor in methyl cyanide than is copper nitrate.

Absorption Spectra of Copper Perchlorate Solutions.—Solutions of copper perchlorate in ethyl acetate and methyl cyanide are emerald-green and blue-green respectively; the following Table lists $\lambda_{\text{max.}}$ and $\varepsilon_{\text{max.}}$ in the visible region. The corresponding values for copper nitrate are also given.[7] As all these solutions obey Beer's Law within the limits of experimental error, the difference in extinction coefficient in methyl cyanide cannot be interpreted by the dissociation equilibrium (6), but suggests that the nitrate ion associates more closely with the copper ion than does the perchlorate ion; these results will be further discussed elsewhere.

		EtOAc	MeCN			EtOAc	MeCN
$Cu(ClO_4)_2$	$\lambda_{\text{max.}}$ (mμ)	820	750	$Cu(NO_3)_2$	$\lambda_{\text{max.}}$ (mμ)	820	850
	$\varepsilon_{\text{max.}}$ (l. mole^{-1} cm.$^{-1}$)	51·4	22·4		$\varepsilon_{\text{max.}}$ (l. mole^{-1} cm.$^{-1}$)	51·6	47·0

Above 200 mμ a solution of copper perchlorate should be transparent, as the perchlorate ion does not absorb in this region. The solutions of copper perchlorate always contain less than 1% of nitrate ion, and this resulted in a weak absorption in the range 295—325 mμ.

Properties of the Copper Perchlorate–Organic Solvent Complexes.—The products of concentrating the solutions of copper perchlorate in ethyl acetate and methyl cyanide have been shown to be $Cu(ClO_4)_2,2{\cdot}5EtOAc$ (m. p. 42°) and $Cu(ClO_4)_2,4CH_3{\cdot}CN$ (m. p. 196°), respectively. The very low m. p. of the former complex explains why it is so difficult to crystallise, and also suggests that it is likely to be more of a lattice complex than a true co-ordination complex, in which the ethyl acetate molecules are only weakly co-ordinated to the copper ions. This is consistent with the accepted ideas that ethyl acetate is a much weaker co-ordinating ligand than methyl cyanide.

Both these complexes were heated under a vacuum in an attempt to remove the organic material; this was carried out at a low temperature to minimise decomposition of the perchlorate. With the methyl cyanide complex, heating under vacuum for 24 hr. at 70°

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[8] Fuoss and Kraus, *J. Amer. Chem. Soc.*, **1933**, **55**, 21.

resulted in the loss of two of the four molecules of cyanide without any decomposition of the copper perchlorate, but further heating decomposed the perchlorate, without complete removal of all the organic material. The partially decomposed material was incompletely soluble in water and contained a small amount of free chloride ion. The decomposition of these complexes to give chloride ion agrees with Monnier's observations [9] on the thermal decomposition of copper perchlorate mono(diethyl ether), which at 180° decomposes into cupric chloride dihydrate.

Infrared Spectra of the Copper Perchlorate Complexes.—The main infrared absorption frequencies of the copper perchlorate complexes are given in the accompanying Table.

Infrared absorption spectra of copper perchlorate complexes.

$Cu(ClO_4)_2,4CH_3{\cdot}CN$		$Cu(ClO_4)_2,2{\cdot}5EtOAc$	
2325 } split	958 ms	1685 } s, split	1185 } b, s
2315	937 ms	1625	1165
	930 w.sh		1090
1465 s } Nujol		1460 s } Nujol	1005
1380 s	800 w	1380 s	
	727w Nujol		
1125 vs		1340 s	927 ms
1067 w.sh			860 s
1038 w.sh			800 w
			727 w Nujol

(vs = very strong, s = strong, b = broad, ms = medium strong, w = weak, w.sh = weak shoulder.)

The chief features are a broad, strong absorption over the range 1185—1000 cm.$^{-1}$ and a sharp peak at 930 cm.$^{-1}$; the former is the characteristic ν_3 frequency of a perchlorate ion, and the latter is the ν_1 frequency, which, although forbidden in the infrared region of a perchlorate ion, occurs weakly in a number of ionic perchlorates,[10] probably owing to slight distortions of the ion in a crystal field of lower symmetry than itself. The occurrence of strong absorptions at this frequency in the above complexes suggests that this frequency has become allowed, so is consistent with the perchlorate ion's changing from an ionic (T_d) to a covalently bonded (C_{3v}) group $-OClO_3$. This change in spectrum has been observed in the infrared spectrum of anhydrous copper perchlorate; these results will be more fully discussed elsewhere. In the methyl cyanide complex the formula alone suggests that the copper ions are probably four co-ordinated with respect to the methyl cyanide molecules, with the oxygen atoms of two separate perchlorate ions making up the co-ordination number of the copper ion with two very long copper–oxygen bonds. Unfortunately, attempts to obtain evidence that this complex is unimolecular in an inert solvent, such as nitromethane, were unsuccessful, as the methyl cyanide molecules were displaced and a copper perchlorate bisnitromethane complex was precipitated.

The split absorption at 2300 cm.$^{-1}$ in the methyl cyanide complex is due to the $-C{\equiv}N$ vibration of the methyl cyanide molecule; this is shifted to slightly higher frequencies in the complex than the normal absorption of the $-C{\equiv}N$ vibration at 2248 cm.$^{-1}$, but this is consistent with the methyl cyanide molecule's being co-ordinated to the copper ions.[7,11] The strong absorption at 1685—1620 cm.$^{-1}$ in the ethyl acetate complex is the normal carbonyl stretching frequency (1750—1735 cm.$^{-1}$) displaced owing to co-ordination of the ester to the copper ions by the oxygen of the carbonyl groups. The strong absorptions at 1340 and 860 cm.$^{-1}$ have not been clearly assigned, but as they have not been observed in any other spectra of simple or complex perchlorates they are assumed to arise from the ethyl acetate molecule.

Attempts to prepare Anhydrous Copper Perchlorate.—Solutions of copper perchlorate in an organic solvent prepared as described above are of interest as potential sources of

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[9] Monnier, *Ann. Chim.*, 1957, **2**, 32.

[10] Miller and Wilkins, *Analyt. Chem.*, 1952, **24**, 1253.

[11] Coerver and Curren, *J. Amer. Chem. Soc.*, 1958, **80**, 3522.

anhydrous copper perchlorate, but attempts to precipitate this (or a readily decomposed complex) by addition of a variety of compounds all failed, as shown below.

Solids. Ammonium and tetraethylammonium perchlorate are insoluble even in boiling ethyl acetate, but the latter salt is soluble in methyl cyanide; however, its addition to solutions of copper perchlorate failed to produce any precipitate.

Liquids. Addition of organic solvents such as n-hexane and ether precipitated the respective copper perchlorate complexes; benzene produced no precipitation. Addition of liquid dinitrogen tetroxide results in an immediate precipitation of nitrosyl perchlorate:

$$Cu(ClO_4)_2 + 2N_2O_4 \longrightarrow Cu(NO_3)_2 + 2NOClO_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Liquid chlorine heptaoxide, anhydrous perchloric acid, and liquid sulphur dioxide are miscible with the copper perchlorate solutions but cause no precipitation even on cooling.

Gases. Sulphur dioxide, carbon dioxide, and carbon monoxide have no effect when bubbled through the copper perchlorate solution, chlorine dioxide changes the emerald-green colour of the solution to leaf-green, and chlorine turns it brown, but there is no precipitation. Ammonia produces an immediate precipitate of tetra-amminecopper perchlorate, but the ammonia cannot be removed from this complex without decomposition of the perchlorate.

EXPERIMENTAL

Preparation of Nitrosyl Perchlorate.[12]—Oxides of nitrogen, prepared by adding concentrated nitric acid dropwise to solid sodium nitrite, were passed into 70% perchloric acid, and the precipitated nitrosyl perchlorate was filtered off on a sintered-glass filter-stick closed by phosphorus pentoxide guard-tubes, and sucked as dry as possible. The product was stored damp but before each experiment approximately 2 g. of nitrosyl perchlorate were transferred to a filter-stick and washed repeatedly with dry ethyl acetate in 10 ml. portions, and the solid was sucked dry between each addition of the solvent until a free-flowing powder was obtained.

Reaction of Copper with Suspensions of Nitrosyl Perchlorate.—The dry nitrosyl perchlorate was transferred directly to a clean, dry 250-ml. B24 round-bottom flask closed by a phosphorus pentoxide guard-tube, and a piece of freshly abraded copper sheet (50 × 10 × 1 mm.) was added. Approximately 30 ml. of dry organic solvent were added, as quickly as possible to avoid access of moisture, and the flask was then evacuated through the guard-tube. The reaction was complete with methyl cyanide in 2—3 hr., but up to 7 hr. were required with ethyl acetate. The final solution was filtered through a No. 4 sintered-glass filter-stick to remove residual nitrosyl perchlorate and a trace of copper metal. In the reaction with methyl cyanide a certain amount of copper perchlorate tetra(methyl cyanide) complex crystallised out as the reaction proceeded; this was either filtered off or redissolved by addition of more methyl cyanide before filtration.

Analysis of Solutions.—A measured volume of the prepared solution was diluted with water, and the aqueous solution then boiled to remove the organic solvent and made up to a known volume; aliquot volumes were then taken for analysis. Copper was estimated gravimetrically as copper ethylenediamine mercuri-iodide,[13] total nitrate and perchlorate gravimetrically as the nitron salts, and nitrate by reduction and a micro-Kjeldahl procedure. Analysis of the solutions obtained as above gave the following typical results. With ethyl acetate: (*a*) at atmospheric pressure, empirical formula $Cu(ClO_4)_{1\cdot60}(NO_3)_{0\cdot40}$; (*b*) under reduced pressure, empirical formula $Cu(ClO_4)_{1\cdot96}(NO_3)_{0\cdot04}$. With methyl cyanide under reduced pressure: empirical formula $Cu(ClO_4)_{1\cdot97}(NO_3)_{0\cdot03}$.

Analysis of Copper Perchlorate Complexes.—*Copper perchlorate tetra(methyl cyanide)* [Found: Cu, 14·8; ClO_4, 45·6. $Cu(ClO_4)_2,4CH_3{\cdot}CN$ requires Cu, 14·9; ClO_4, 46·6%]. *Copper perchlorate* 2·5-*ethyl acetate* [Found: Cu, 12·2; ClO_4, 38·25. $Cu(ClO_4)_2,2{\cdot}5CH_3{\cdot}CO_2C_2H_5$ requires Cu, 12·3; ClO_4, 38·5%]. *Copper perchlorate bisnitromethane* [Found: Cu, 16·7; ClO_4, 52·9. $Cu(ClO_4)_2,2CH_3{\cdot}NO_2$ requires Cu, 16·5; ClO_4, 53·1%]. The infrared spectrum of this complex showed no cyanide band at 2300 cm.$^{-1}$ but a band at 1550 cm.$^{-1}$ due to the nitro-group.

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[12] Hofmann and Zedtwitz, *Ber.*, 1909, **42**, 203.

[13] Vogel, " Text Book of Quantitative Inorganic Analysis," Longmans, Green and Co., London, 2nd edn., 1951, p. 433.

Molecular-weight Determinations.—These were carried out ebullioscopically using a Swietoslawski differential ebulliometer [14] reduced to a 10 ml. volume. All determinations were carried out behind blast screens.

Electrical Conductivities.—These were measured by using a Cambridge conductivity apparatus involving a 1000 c./sec. oscillator and a galvanometer as a null-point instrument. The cell design was that of Groeneveld and Zuuv,[15] which enables measurements to be made on hygroscopic solutions under a dry atmosphere. The methyl cyanide and ethyl acetate were dried and purified by repeated fractionation off phosphorus pentoxide until the specific conductivities were less than 10^{-7} ohm^{-1} cm.$^{-1}$.

Measurement of Spectra.—The visible and ultraviolet spectra were measured on a Unicam S.P. 500 Spectrophotometer using 1-mm. silica cells. The infrared spectra were determined as Nujol mulls in a Unicam S.P. 100 Spectrophotometer.

The authors are indebted to Dr. G. W. Gray for the infrared measurements, to the Chemical Society for a grant for apparatus, and to the Department of Scientific and Industrial Research for a maintenance grant (to A. E. U.).

THE UNIVERSITY, HULL. [*Received, November 24th,* 1959.]

[14] Swietoslawski, " Ebulliometric Measurements," Reinhold, New York, 1945, pp. 11, 18, 28.

[15] Groeneveld and Zuuv, *Rec. Trav. chim.*, 1953, **72**, 618.