

σ -Bonded Organotransition-metal Ions. Part V.† The Formation of Mono- and Di-halogenomethylchromium(III) Ions and their Reaction with Mercuric Nitrate

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Air-stable dihalogenomethylchromium(III) ions are the main products of reduction of chloroform, bromoform, and iodoform with less than two equivalents of chromous perchlorate or fluoroborate. With four or more equivalents of chromous perchlorate the main products are the corresponding air-stable monohalogenomethylchromium(III) ions. Methylchromium(III) ion cannot be detected in the products. These six organochromium(III) ions react with mercuric nitrate; the monochloro- and monobromo-methylchromium(III) ions lead to the corresponding monohalogenomethylmercury(II) ions, in good yield, through attack of mercury(II) on carbon, but in the other four cases the main product is mercurous ion formed after attack of mercury(II) on halogen. The mechanisms of the reduction processes are discussed in relation to the corresponding reductions with chromous sulphate and chloride, from which stable organochromium ions cannot be obtained.

THE displacement of chromium(III) and other transition-metal ions from σ -bonded organotransition-metal ions is a potentially valuable method of preparing organomercury compounds. For example, benzyl-¹ and pyridiomethyl-mercuric halides² can be prepared almost quantitatively from the corresponding organochromium(III) ions. However, although it has been reported that mercuric chloride does not react with the dichloromethylchromium(III) ion,³ we expected that mercuric nitrate, being some forty times more reactive than mercuric chloride towards this type of substrate, might yield the dichloromethylmercuric ion. Our initial experiments resulted in the quite unexpected monochloromethylmercuric salt, which precipitated on adding chloride ion. This Paper therefore describes further investigations into the identity of the halogenomethylchromium(III) species present in the products of reduction of halogenoforms by chromous perchlorate, and their reaction with mercuric salts.

RESULTS

Reaction of Halogenoforms with Chromous Perchlorate.—The reaction of one equivalent of 0.5M-chromous perchlorate in 0.5M-perchloric acid with one equivalent of chloroform in aqueous acetone in absence of air led to the slow formation of a red solution. After 2 hr. air was admitted and the acetone was removed *in vacuo*. Cation-exchange chromatography of the solution gave, on elution with 1M-perchloric acid, two main fractions corresponding almost exactly to those described by Anet,³ *i.e.*, the green chloropenta-aquochromium(III) ion, followed by the red solution *A* described in Table 1; 5M-perchloric acid eluted the violet hexa-aquochromium(III) ion. With four or with six equivalents of chromous perchlorate, solution *A* was not evident; instead another red solution *B*, described in Table 1, was obtained, and the green dinuclear-bridged-chromium(III) ion,⁴ formed by air-oxidation of the excess of chromous ion, remained on the column.

Similar reduction of bromoform, with one, four, and six equivalents of chromous ion gave solutions *C*, *D*, and *D*, respectively. Similar reduction of iodoform gave solu-

tions *E*, *F*, and *F*, respectively, though complete separation of solution *E* from the hexa-aquochromium(III) ion was not achieved. The main characteristics of the red solutions *C*, *D*, *E*, and *F* are shown in Table 1. The extinction coefficients for the solution *E* are the least accurate because of the uncertainty in the analysis.

The red solutions (*A*–*F*) are all stable to air and in 1M-perchloric acid for many hours (solutions *A*, *C*, and *E*) or for many days (solutions *B*, *D*, and *F*).

Reduction of Methylene Dihalides.—Reaction of methylene di-iodide with one equivalent of chromous perchlorate at room temperature and of methylene dibromide with one equivalent of chromous perchlorate for 1 hr. at 50° (or for several hours at room temperature) gave the red solutions *D* and *F*, respectively.

Reduction of Carbon Tetrachlorides.—Reduction of carbon tetrachloride with one equivalent of chromous perchlorate gave an unstable red solution, believed to contain the trichloromethylchromium(III) ion,³ which decomposed in the presence of oxygen or an excess of chromous ion within a few minutes, but not to further organochromium(III) ions. The corresponding reduction of carbon tetrabromide gave a similar red solution believed to contain the tribromomethylchromium(III) ion. In the absence of air or an excess of chromous perchlorate the solution was stable for several hours, but on addition of an excess of chromous ion it was destroyed without the formation of further organochromium(III) ions. It was rapidly destroyed by oxygen.

Reactions of the Organochromium Ions.—(a) *Silver nitrate.* All the red solutions failed to precipitate silver halide in the cold, but on warming with an excess of silver nitrate, all precipitated the silver halide (not elemental silver) and the hexa-aquochromium(III) ion remained in solution.

(b) *Mercuric nitrate.* All the red solutions reacted with mercuric nitrate. Whereas the reaction with monochloromethylchromium(III) ion (*ca.* 2×10^{-2} M) took only a few seconds, that with the dichloromethylchromium(III) ion was some 1000 times slower. The di- and mono-iodomethylchromium(III) ions reacted almost instantaneously. The chromatographed solutions were too dilute for preparative studies; however, the bulk solutions before chromatography also reacted with an excess of mercuric nitrate.

² R. G. Coombes and M. D. Johnson, *J. Chem. Soc. (A)*, 1966, 1805.

³ F. A. L. Anet, *Canad. J. Chem.*, 1959, **37**, 58.

⁴ M. Ardon and R. A. Plane, *J. Amer. Chem. Soc.*, 1959, **81**, 3197; R. W. Kalaczkowski and R. A. Plane, *Inorg. Chem.*, 1964, **3**, 322.

† Part IV, M. D. Johnson, M. L. Tobe, and Lai-Yoong Wong, *J. Chem. Soc. (A)*, 1967, 491.

¹ F. A. L. Anet and E. Leblanc, *J. Amer. Chem. Soc.*, 1957, **79**, 2649.

On adding sodium chloride or bromide such that no mercuric halide would be precipitated, solution *B* gave a copious white precipitate of monochloromethylmercuric chloride and bromide, respectively, whereas solution *A* gave only a trace of these compounds. Similar reactions of solution *D* gave white precipitates of monobromomethylmercuric chloride and bromide, respectively, both contaminated with mercurous halide, but solution *C* gave almost entirely mercurous salt with traces of monobromomethylmercuric halides. Solutions *E* and *F* reacted with mercuric nitrate followed by chloride ion to give only mercurous salts.

Reaction of diazomethane with mercuric nitrate. On addition of ethereal diazomethane to aqueous mercuric nitrate, nitrogen was evolved, but no precipitate formed. On addition of chloride ion to the aqueous solution, the precipitate was mercurous chloride.

DISCUSSION

Chromous perchlorate was used as the reducing agent because it is known that, whilst chromous chloride^{5,6} and chromous sulphate⁷ will reduce the halogenoforms,

additional evidence is provided by the fact that the monobromomethylchromium(III) ion, as identified by ultraviolet spectra and products of reaction with mercuric nitrate, is also formed by reduction of methylene dibromide with chromous perchlorate.

The results for the reduction of iodoform are a little less certain, because of the poor separation of the diiodomethylchromium(III) ion from the hexa-aquo-chromium(III) ion. However, as the same solution (*F*) is obtained from the reduction of iodoform with four equivalents of chromous ion and from methylene diiodide with one equivalent of chromous ion, and these gave *ca.* 1 : 1 chromium : iodide analyses, there can be little doubt that the red doubly charged ion in solution *F* is the monoiodomethylchromium(III) ion. Similarly, as solution *E* is patently different from solution *F* and contains a doubly charged ion that can be reduced to the monoiodomethylchromium(III) ion, it must contain the di-iodomethylchromium(III) ion. Unfortunately,

TABLE I
Solutions obtained from the reduction of halogenoforms with chromous perchlorate

Halogenoform	Product solution	Halogen : chromium ratio	Structure	Ultraviolet spectra λ_{\max} $\mu\mu$ (log ϵ)		
CHCl ₃	<i>A</i>	1.8 ± 0.2 : 1	CHCl ₂ Cr ²⁺	265 (3.39)	396 (2.06)	514 (1.36)
CHCl ₃	<i>B</i>	0.96 ± 0.1 : 1	CH ₂ ClCr ²⁺	262 (3.54)	391 (2.31)	517 (1.30)
CHBr ₃	<i>C</i>	2.0 ± 0.1 : 1	CHBr ₂ Cr ²⁺	280 (3.71)	401 (2.26)	521 (1.65)
CHBr ₃	<i>D</i>	1.0 ± 0.1 : 1	CH ₂ BrCr ²⁺	267 (3.42)	397 (2.16)	520 (1.34)
CHI ₃	<i>E</i>	0.4 ± 0.2 : 1	CHI ₂ Cr ²⁺	281 (3.2)	324 (3.0)	415 (2.3) ^a
			and Cr(H ₂ O) ₆ ³⁺			538 (1.7)
CHI ₃	<i>F</i>	0.82 ± 0.2 : 1	CHI ₂ ICr ²⁺	264 (3.34)	396 (2.42)	295 (3.37) 524 (1.42)

^a Shoulder.

they do not apparently lead to stable organochromium species. We have shown that chromous fluoroborate leads also to stable organochromium species.

The reaction of chloroform with a deficiency of chromous perchlorate proved almost identical with that described by Anet.³ Our analysis, which is in agreement with Anet's, confirms the presence of the penta-aquodichloromethylchromium(III) ion in solution *A*. That solution *B* reacts with mercuric nitrate at a greatly different rate from solutions containing a similar concentration of the dichloromethylchromium(III) ion, gives different products (notably the monochloromethylmercuric ion), has a different ultraviolet spectrum from the dichloromethylchromium ion and a chlorine:chromium ratio of 1 : 1, shows clearly that it contains the monochloromethylchromium(III) ion. The double charge on this ion is confirmed by its position of elution from the ion-exchange resin.⁸

The results from the reduction of bromoform correspond very closely to those from chloroform, and the evidence that solutions *C* and *D* contain the dibromomethylchromium(III) and the monobromomethylchromium(III) ions, respectively, is the same. However,

⁵ T. Kiba and K. Terada, *J. Chem. Soc. Japan*, 1954, **75**, 196.

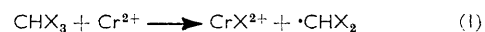
⁶ H. Lux, D. Sarre, and I. Schaffelhofer, *Chem. Ber.*, 1964, **97**, 2301.

⁷ C. E. Castro and W. C. Kray, *J. Amer. Chem. Soc.*, 1966, **88**, 4447.

the corresponding halogenomethylmercuric salt could not be obtained from either of these solutions.

Attempts were also made to detect the methylchromium(III) ion in the products of reaction of an excess of chromous ion with all three halogenoforms. No conclusive evidence could be detected in any of the products of reaction of mercuric salts and halide ion with any of the red solutions or of the bulk reaction solutions. It was confirmed that methyl iodide does not visibly react with chromous perchlorate during 1 hr. at 80°.

Mechanism.—Reduction. The first stage of the reduction of the halogenoforms and of the methylene dihalides corresponds to that suggested for many reactive organic halides;^{3,7,9,10} *i.e.*, the abstraction of a halogen atom by chromous ion to give an organic radical which is captured by a further chromous ion as shown in equations (1) and (2). The further reaction of the



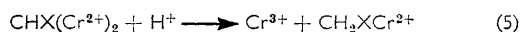
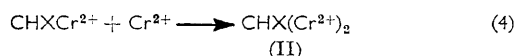
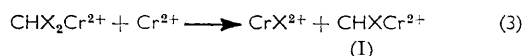
dihalogenomethylchromium(III) ions to monohalogenomethylchromium(III) ions has no precedent, but may

⁸ E. L. King and E. B. Dismukes, *J. Amer. Chem. Soc.*, 1952, **74**, 1674.

⁹ J. K. Kochi and D. D. Davis, *J. Amer. Chem. Soc.*, 1964, **86**, 5264.

¹⁰ R. G. Coombes, M. D. Johnson, and N. Winterton, *J. Chem. Soc.*, 1965, 7029.

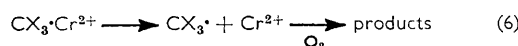
be accommodated within the mechanism suggested for the reduction of chloroform by chromous sulphate.⁷ Probably chromous ion abstracts a further halogen atom and the resulting chromous ion-methylene complex (I) is captured by a further chromous ion to give a dichromium(III) complex (II) as in equations (3) and (4). Acid-catalysed decomposition of the dichromium complex would then give the monohalogenomethylchromium(III) ion and the hexa-aquochromium(III) ion as in equation (5). (The alternative mechanism in



which the chromous ion *displaces* a halogen atom, in each stage, has not been disproved in all metal-ion reductions of organic halides, but is unlikely in view of generality of peripheral halogen abstractions in the free-radical chemistry of alkyl halides.)

This mechanism is supported as follows: the order of reactivity $\text{I} > \text{Br} > \text{Cl}$ for both stages is that expected for the halogen abstraction from halogenoform or the dihalogenomethylchromium ion. The chromous ion-methylene complex (I) can be considered as a chromium(III) complex of the organic radical on $\text{CHX}\cdot$, and has also been suggested as an intermediate in the reduction of halogenoforms by chromous sulphate.⁷ For the latter reaction, Castro and Kray suggested that equations (4) and (5) be combined, without the intervention of the dichromiumalkyl (II), as a route to further transient halogenomethylchromium ions, but the dichromium species (II) is analogous to the well-established aquo-, hydroxo-,⁴ amino-,¹¹ and thiocyanato-bridged¹² dichromium species and is likely to be sufficiently stable to be an intermediate.

The tribromo- and trichloro-methylchromium(III) ions are not reduced to the dihalogenomethylchromium(III) ions by an excess of chromous ion, and a different mechanism of reduction must be involved; probably through the reversible homolytic fission of the carbon-chromium bond (equation 6), which is known to occur in other cases where the organic radical is relatively stable.¹³ In the presence of oxygen, both the tribromo-methyl radical and the chromous ion are rapidly oxidised, and their recombination to the organochromium ion is suppressed. Thus the tribromo- is much more stable than the trichloro-methylchromium(III) ion, because the trichloro- is more stable and is formed more rapidly than the tribromo-methyl radical.



Displacement of chromium by mercury. The mono-

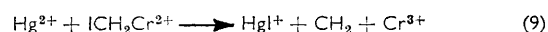
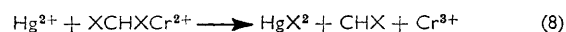
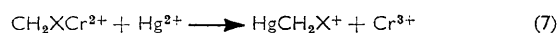
¹¹ M. Ardon and B. E. Mayer, *J. Chem. Soc.*, 1962, 2816.

¹² D. L. Ball and E. L. King, *J. Amer. Chem. Soc.*, 1958, **80**, 1091.

¹³ R. G. Coombes and M. D. Johnson, *J. Chem. Soc. (A)*, 1966, 177.

chloro- and monobromo-methylmercuric salts are almost certainly formed through the bimolecular displacement of chromium by attack of the mercury on the carbon atom as in equation (7). This is supported as follows: (i) the rate of displacement in dilute solution is much slower than in concentrated solutions and increases with the concentration of the mercuric salt; (ii) the inorganic product is the hexa-aquochromium(III) ion; and (iii) by analogy with the detailed studies on analogous displacement reactions.² No effort was made to maximise the yields of the halogenomethylmercuric halides, which were *ca.* 50%, but the method is clearly of preparative value and much simpler, at least for monobromomethylmercuric chloride, than that so far described.¹⁴ Monochloromethylmercuric bromide had not been reported previously.

On the other hand since the reaction of mercuric nitrate with dihalogenomethyl- and monoiodomethylchromium(III) ions does not give the corresponding halogenomethylmercuric salts, though it does liberate the hexa-aquochromium(III) ion, there must be an alternative mode of reaction, *i.e.*, electrophilic attack of mercury on halogen rather than on carbon, as in equations (8) and (9). This is supported as follows: (i) by the order of reactivity ($\text{CHI}_2\text{Cr}^{2+} > \text{CH}_2\text{ICr}^{2+} > \text{CHBr}_2\text{Cr}^{2+} > \text{CHCl}_2\text{Cr}^{2+}$); (ii) the reaction is of the first order in mercuric nitrate and in organochromium ion; and (iii) by the formation of mercurous ion during the reaction. The order of reactivity $\text{I} > \text{Br} > \text{Cl}$ is as predicted from the stability constants of the mercuric halide being formed,¹⁵ and the order dihalogenomethylchromium(III) $>$ monohalogenomethylchromium(III) is due to the greater stability of monohalogenomethylenes than methylene itself.¹⁶ The formation of mercurous ion is almost certainly the result of further reaction of the intermediate methylene with the excess of mercuric nitrate, for we have shown that diazomethane (a methylene precursor) also rapidly reduces mercuric to mercurous nitrate (equation 10). This was somewhat unexpected in view of the ready reaction of diazomethane with mercuric chloride, even in wet ether, to give monochloromethylmercuric chloride.¹⁷ Formaldehyde, that might have been produced through hydrolysis of the intermediate monohalogenomethylenes, was shown to be too slow a reducing agent to be effective in these reactions.



¹⁴ R. Kh. Freidlina and F. K. Velichko, *Izvest. Acad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1959, 1225.

¹⁵ G. B. Deacon, *Rev. Pure Appl. Chem. Australia*, 1963, **13**, 189.

¹⁶ W. E. Parham and E. E. Schweizer, *Org. Reactions*, 1963, **13**, 55.

¹⁷ L. Hellerman and M. D. Newman, *J. Amer. Chem. Soc.*, 1932, **54**, 2859.

EXPERIMENTAL

Chromous Ion Solutions.—Chromous perchlorate was prepared from chromium metal (Koch-Light chromium flake 99.99%) by the method of Crabtree.¹⁸ Chromous fluoroborate was made similarly.

Reduction of Halogenoforms to Dihalogenomethylchromium(III) Ions.—Chloroform (1 ml.) was introduced gradually into nitrogen-flushed acetone (100 ml.) and 0.5M-chromous perchlorate in 0.5M-perchloric acid (25 ml., 1 equiv.) was added, with stirring, under nitrogen. Within several minutes the solution became red; after 2 hr. the acetone and excess of chloroform were removed *in vacuo*. The solution was separated by ion-exchange chromatography, described below, to give a red solution of the penta-aquodichloromethylchromium(III) ion³ (characteristics in Table 1).

Similar reaction of bromoform (1 ml.) with 0.5M-chromous perchlorate (23 ml., 1 equiv.) for 10 min. gave, after ion-exchange chromatography, a red solution of the *penta-aquodibromomethylchromium(III) ion* (Table 1).

Similar reaction of iodoform (2.96 g.) with 0.5M-chromous perchlorate (20 ml., 1 equiv.) for 5 min. gave, after filtration off of unchanged iodoform and ion-exchange chromatography, a red solution of the *penta-aquodi-iodomethylchromium(III) ion* (Table 1).

Reduction of Halogenoforms to Monohalogenomethylchromium(III) Ions.—Chloroform (0.5 ml.) was treated as above with 0.5M-chromous perchlorate (50 ml., 4 equiv.) for 3½ hr. Ion-exchange chromatography of the product solution gave a red solution of the *penta-aquomonochloromethylchromium(III) ion* (Table 1).

Similar reaction of bromoform (0.5 ml.) with 0.5M-chromous perchlorate (46 ml., 4 equiv.) for ¼ hr. gave, after ion-exchange chromatography, a red solution of the *penta-aquomonobromomethylchromium(III) ion* (Table 1). Chromous fluoroborate was used with equal success in this preparation.

Similar reaction of iodoform (1.98 g.) with 0.5M-chromous perchlorate (40 ml., 4 equiv.) for 10 min. gave, after ion-exchange chromatography, a red solution of the *penta-aquomonoiodomethylchromium(III) ion* (Table 1).

Reduction of Methylene Dihalides.—Methylene dibromide (1 ml.) was treated as above with 0.5M-chromous perchlorate (29 ml., 1 equiv.) for 20 hr. Ion-exchange chromatography gave a red solution of the penta-aquomonobromomethylchromium(III) ion.

Similar reaction of methylene di-iodide (1 ml.) with 0.5M-chromous perchlorate (25 ml., 1 equiv.) for ¼ hr. gave, after ion-exchange chromatography, a red solution of the penta-aquomonoiodomethylchromium(III) ion.

Reduction of Carbon Tetrahalides.—Carbon tetrachloride (1 ml.) was treated as above with 0.5M-chromous perchlorate (21 ml., 1 equiv.). A red solution formed almost immediately but became green during several minutes;³ bubbling air through the red solution did not noticeably increase the rate of decomposition.

Similar reaction of carbon tetrabromide (3.32 g.) with 0.5M-chromous perchlorate (20 ml., 1 equiv.) gave a very red solution immediately. The colour was stable for several hours under nitrogen but was rapidly destroyed by air and by an excess of chromous ion, in each case giving green solutions.

Separation of Organochromium Ions.—Portions of bulk

solutions as prepared above were separated on a column (15 × 1.5 cm.) of Dowex 50W-X8 at an elution rate of 3 ml. per min. Some halide ions were always initially washed out with water, but neither water nor 0.1M-perchloric acid eluted any chromium ions. 1M-Perchloric acid first eluted the appropriate green halogenopenta-aquochromium(III) ion (although in the iodoform reactions, small amounts of an unknown green ion were produced), followed by the red organochromium species at concentrations of 1—3 × 10⁻³M. Where mixtures were present the monohalogenomethylchromium ions were eluted before the dihalogenomethylchromium ions. 5M-Perchloric acid eluted the violet hexa-aquochromium(III) ion, leaving the green binuclear chromium(III) species on the column.

Chloromethylmercuric Chloride.—To a solution of monochloromethylchromium(III) ion prepared as above, but before ion-exchange chromatography, mercuric nitrate [Hg(NO₃)₂·H₂O, 4.5 g.] in 1M-perchloric acid (20 ml.) was added with stirring. The solution became violet within 1 min. and addition of excess of aqueous sodium chloride (50 ml.) after 5 min. precipitated a white solid (0.8 g.). Except for traces of mercurous chloride, this was entirely chloromethylmercuric chloride (45%).¹⁷ The dried product was extracted with boiling acetone and recrystallised from acetone-water to give white micaceous scales (Table 2).

Chloromethylmercuric Bromide.—To a solution of monochloromethylchromium(III) ion prepared as above, but before ion-exchange chromatography, mercuric nitrate (6.0 g.) in 1M-perchloric acid (50 ml.) was added with stirring. After 4 min. water (500 ml.) was added (to avoid a mercuric bromide precipitate), followed by an excess of aqueous sodium bromide (50 ml.). The white precipitate of *chloromethylmercuric bromide* (1.0 g., 50%) was extracted from traces of mercurous bromide with hot benzene and recrystallised from ethanol, giving white micaceous scales. (Found: C, 3.7; H, 0.6; Br, 25.2; Hg, 60.4. CH₂BrClHg requires C, 3.6; H, 0.6; Br, 24.2; Hg, 60.8%) (Table 2).

Bromomethylmercuric Chloride.—To a solution of monobromomethylchromium(III) ion prepared as above, but before ion-exchange chromatography, mercuric nitrate (6.0 g.) in 1M-perchloric acid (25 ml.) was added with stirring. The solution became red-violet then, within 1 min., violet and some mercuric bromide was precipitated. A slight excess of silver nitrate (2.0 g.) in water (25 ml.) was added to remove bromide ion from the solution (as these interfere by precipitating bromomethylmercuric bromide along with the chloride), and the mercuric bromide redissolved. The mixture was filtered into an excess of aqueous sodium chloride (50 ml.) to give a white precipitate (1.6 g.) which contained bromomethylmercuric chloride, mercurous chloride, and traces of silver chloride. The mixture was extracted with hot benzene to give white crystals of bromomethylmercuric chloride¹⁴ (1.1 g., 57%) which were recrystallised from ethanol (Table 2). The ¹H n.m.r. spectrum indicated a small (5%) impurity, probably formed during recrystallisation, for which chloroform and benzene are to be preferred.

Bromomethylmercuric Bromide.—To a solution of monobromomethylchromium(III) ion prepared as above, but before ion-exchange chromatography, water (1200 ml.) was added (to avoid precipitation of mercuric bromide), followed by mercuric nitrate (6.0 g.) in 1M-perchloric acid (25 ml.). An excess of aqueous sodium bromide (50 ml.) was added after 10 min., with stirring, to give a white

¹⁸ J. M. Crabtree, *J. Chem. Soc.*, 1964, 4647.

TABLE 2
 Monohalogenomethylmercuric halides

Compound	ClCH ₂ HgCl	ClCH ₂ HgBr	BrCH ₂ HgCl	BrCH ₂ HgBr	CH ₃ HgCl	CH ₃ HgBr
M. p.	132°	140—141°	110—112° ^a	126—128°		
M. p. (lit.)	131° ¹⁷	—	118—120° ¹⁴	123—125.5° ¹⁹		
Infrared spectra (cm. ⁻¹) (Nujol mulls)	1164s 1152m 1112m	1156s 1100m	1152wm 1122s 1119s 1060w	1145w 1113s 1051wm		
	776w	723s	720w 708s	719w 698s		
	722s ^b 539w ^c 315s ^d	715s ^b 531vw ^c 218s ^d	639s ^b 514m ^c 313s ^d	637s ^b 510m ^c 214s ^d	546w ^e 315s ^{d,j}	538ms ^{e,i} 214w ^{d,j}
¹ H n.m.r. spectra ^h					8.99 ^e 9.07 ^f 9.16 ^g	8.94 ^e 9.01 ^f 9.09 ^g
τ-CH ₂	7.46	7.41	7.93	7.83		
<i>J</i> (¹⁹⁹ Hg-H) (±1, c./sec.)	124	116	106	102	215 ^e 212 ^f 209 ^g	212 ^e 207 ^f 205 ^g

^a Contains 5% impurity. ^b C-Halogen str. ^c C-Hg str. ^d Hg-Halogen str. ^e In pyridine (J. V. Hatton, W. G. Schneider, and W. Siebrand, *J. Chem. Phys.*, 1963, **39**, 1330). ^f In methanol (M. D. Rausch and J. R. Van Wazer, *Inorg. Chem.*, 1964, **3**, 761). ^g In dioxan (M. D. Rausch and J. R. Van Wazer, *Inorg. Chem.*, 1964, **3**, 761). ^h In benzene. ⁱ P. L. Goggin and L. A. Woodward, *Trans. Faraday Soc.*, 1966, **62**, 1423. ^j G. E. Coates and D. Ridley, *J. Chem. Soc.*, 1964, 166.

precipitate (1.2 g.). This was a mixture of bromomethylmercuric bromide¹⁹ (net yield 37%) with mercurous bromide. The former was extracted with hot benzene and recrystallised from ethanol to give white micaceous scales (Table 2).

Analyses of Organochromium Ions.—An aliquot portion (20—200 ml.) of the chromatographed organochromium solution (10⁻²—10⁻³M) was heated to boiling with an excess of dilute silver nitrate in dilute nitric acid. The precipitated silver halide was filtered off, washed with dilute nitric acid, dried *in vacuo*, and weighed. The violet filtrate, plus washings, was further evaporated and diluted to a known volume (10—50 ml.). The chromium content was

¹⁹ R. Kh. Freidlina, A. N. Nesmayanov, and F. A. Tokareva, *Chem. Ber.*, 1936, **69**, 2019.

²⁰ P. J. Elving and B. Zemel, *J. Amer. Chem. Soc.*, 1957, **79**, 1281.

determined by measuring the optical density at 575 mμ (ε = 13.9²⁰) of the hexa-aquochromium(III) ion formed.

Reaction of Diazomethane with Aqueous Mercuric Nitrate.—Reactants were in such amounts as to simulate a typical reaction of mercuric nitrate with a bulk solution of the organochromium ion. Diazomethane in ether, prepared by the method of de Boer and Backer,²¹ was distilled directly into a large excess of mercuric nitrate (3 g.) in 0.5M-perchloric acid (50 ml.). Some nitrogen was evolved but the colourless solution remained clear. The ether was removed *in vacuo* and an excess of aqueous sodium chloride was added. Only mercurous chloride (0.20 g.) was precipitated.

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²¹ Th. J. de Boer and H. J. Backer, *Rec. Trav. chim.*, 1954, **73**, 229.