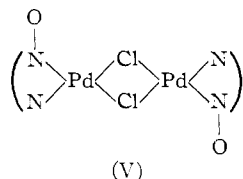by analysis and by its infrared spectrum, which exhibits a strong sharp carbonyl band[12] near 1790 cm.$^{-1}$.

When this acylated palladium(II) complex is treated with dilute, aqueous sodium hydroxide the ester is cleaved and the resulting compound appears to be [Pd(POX)Cl]. This compound probably is dimeric (V).

(V)

The reaction of [Pt(POX)$_2$] with acetyl chloride in chloroform solution produces a substance conforming approximately to the formulation [Pt-(POX–COCH$_3$)$_2$]Cl$_2$. This compound is not so easily purified as [Pd(POX–COCH$_3$)Cl$_2$], and the analyses are not ideal. The infrared spectrum of the product shows the band (at 1780 cm.$^{-1}$) characteristic of the oxime ester, and there seems to be little question that acylation has taken place.

On treatment with acetyl chloride the nickel(II) complex, [Ni(POX)$_2$], undergoes decomposition.

Insofar as the studies reported here reveal, the effect of coördination of an oxime group to a metal ion on the ease of formation and solvolysis of oxime esters and, conversely, the effect of acylation on the

stability and ease of dissociation of the oxime–metal ion bond are in keeping with expectations based on modern concepts of chemistry. Since both the metal ion and the acetyl group are electrophilic toward the oxime function, it is not surprising to find the effects mutually deleterious.

The apparent catalysis of the solvolysis of the oxime ester by metal ions provides an additional example of a type of observation which is rapidly approaching the status of a generalization of *ligand reactions*. At this time, there exist no broadly established generalizations in this realm, despite the fact that certain seemingly obvious generalizations may soon find experimental justification. In the case at hand, the acetyl group represents an uncoördinated bulky function adjacent to a coördinated function. Further, this *dangling* group is attached to the coördinated group by a link which is normally susceptible to solvolytic cleavage. In such circumstances, the lability toward solvolytic cleavage is expected to be enhanced by metal ion coördination so long as the bond undergoing cleavage is not a part of a chelate ring. Eichhorn and Bailar[13] first pointed out an example of this kind among Schiff base complexes.

(12) O. Exner and M. Horak, *Collection Czechoslov. Chem. Comms.*, **24**, 2992 (1959).

(13) G. L. Eichhorn and J. C. Bailar, Jr., This Journal, **75**, 2905 (1953).

The Reaction of Metal Chelates. I. Halogenation of Metal Chelates of 1,3-Diketones[1,2]

By James P. Collman, Robert A. Moss,[3a] Henry Maltz[3b] and Clifford C. Heindel

Received August 1, 1960

Chlorine, bromine and iodine have been substituted directly on the chelate rings of metal chelates of 1,3-diketones. Bromine, iodine monochloride, and the N-halosuccinimides have been used as halogenating agents. Halogenated chelates containing chromium, cobalt, aluminum, iron and copper have been prepared by these direct substitution processes.

The chemical literature reveals many studies of metal acetylacetonates; however, these researches have focused on the physical properties, stereochemistry, bonding and synthesis of these chelates.[4] Very few reports record the chemical reactions of metal acetylacetonates.

Of the scattered reports concerning the chemical reactions of metal chelates, only a few describe processes in which the chelate molecule was altered, but the chelate rings were not destroyed. Chlorination of copper phthalocyanine yielded a hexadeca-

chlorinated copper phthalocyanine.[5] The copper chelate of 2-hydroxy-1-naphthaldehyde reacted with aqueous methylamine to form *cis* and *trans* isomers of the chelate of the N-methylimine.[6]

The first example of the direct substitution of a metal acetylacetonate is the reported bromination of chromium(III) acetylacetonate (I) by the action of bromine in chloroform.[7] The product of this reaction was reported to be tris-(3-bromo-2,4-pentanediono)-chromium(III) (II), but this substance was not fully characterized. Another isolated example of this type of reaction was reported recently.[8] Treatment of copper acetylacetonate (XIII) with N$_2$O$_4$ yielded a complex which was

(1) Presented at the 137th Meeting of the American Chemical Society, Cleveland, Ohio, April, 1960.

(2) This work was supported in part by the Petroleum Research Fund administered by the American Chemical Society, by the Research Corporation and by the Faculty Research Council of the University of North Carolina.

(3) National Science Foundation Summer Undergraduate Fellows, (a) 1959; (b) 1960.

(4) A. E. Martell and M. Calvin, "Chemistry of Metal Chelate Compounds," Prentice–Hall, Inc., New York, N. Y., 1952.
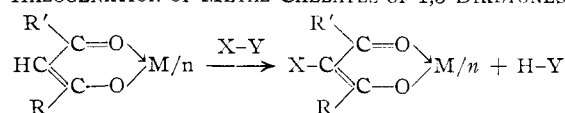
(5) M. Shigemitsu, *J. Chem. Soc. Japan, Ind. Chem. Soc.*, **62**, 112 (1959).

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(7) H. Reihlen, R. Illig and R. Wittig, *Ber.*, **58B**, 12 (1925).

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TABLE I

HALOGENATION OF METAL CHELATES OF 1,3-DIKETONES

$$R' \diagdown C=O \diagdown \quad R' \diagdown C=O \diagdown$$
$$HC \diagup \diagdown C-O \diagup M/n \xrightarrow{X-Y} X-C \diagup \diagdown C-O \diagup M/n + H-Y$$
$$R \diagup \qquad R \diagup$$

Unsubstit. chelate	Halogenated chelate	R	R'	M	n	X-Y[a]	Solvent	Yield,[b] %	Infrared band[c] of halogenated chelate, cm.$^{-1}$
I	II	CH₃	CH₃	Cr	3	Br₂	HOAc	64	1540
I	II	CH₃	CH₃	Cr	3	NBS	HOAc	60	1540
I	III	CH₃	CH₃	Cr	3	ICl	HOAc	72	1530
I	III	CH₃	CH₃	Cr	3	NIS	HOAc	62	1530
I	IV	CH₃	CH₃	Cr	3	NCS	HOAc	65	1550
V	VI	CH₃	CH₃	Co	3	Br₂	HOAc	53	1545
V	VI	CH₃	CH₃	Co	3	NBS	CHCl₃	84	1545
V	VII	CH₃	CH₃	Co	3	ICl	HOAc	97	1535
V	VII	CH₃	CH₃	Co	3	NIS	CHCl₃	42	1535
V	VIII	CH₃	CH₃	Co	3	NCS	HOAc	49	1545
IX	X	CH₃	C₆H₅	Cr	3	NBS	CHCl₃	46	1530
XI	XII	C₆H₅	C₆H₅	Cr	3	NBS	CHCl₃	65	1520
XIII	XIV	CH₃	CH₃	Cu	2	NCS	CHCl₃	78	1555
XV	XVI	CH₃	CH₃	Al	3	NBS	CHCl₃	58	1560
XVII	XVIII	CH₃	CH₃	Fe	3	NBS	CHCl₃	55	1545

[a] X-Y is the halogenating agent; NCS, NBS and NIS represent N-chloro, N-bromo and N-iodosuccinimide. [b] This yield is based on the unsubstituted chelate. [c] Only the strong bands from 1600 to 1500 cm.$^{-1}$ are indicated.

designated as bis-(3-nitro-2,4-pentanediono)-copper (II); however, the structure of this chelate was not rigorously established.

In this Laboratory, a detailed investigation of the reactions of metal chelates, particularly acetylacetonates, has begun. These chelates will be considered as sensitive organic heterocycles and the effect of coördination on the chemical properties of the organic ligand will be investigated. It is hoped that such studies will lead to the fabrication of a wide variety of new chelates. In particular, studies of the elaboration of stable chelates may make possible the preparation of monomers containing coördinated metal atoms.

Consideration of the proposed aromaticity[9,10] of certain metal acetylacetonates suggested that these molecules might undergo electrophilic substitution. Halogenation seemed the best starting point to investigate this hypothesis. The halogenation of metal acetylacetonates and the properties of the halogenated chelates are described below.

The instability of copper(II) acetylacetonate (XIII) precludes the use of this and similarly acid labile chelates in the presence of such strongly electrophilic media as bromine. The copper(II) complexes of 3-ketoaldehydes have been reported to break down in the presence of bromine in chloroform.[11] Aryl acid halides also break down copper acetylacetonate in chloroform.[12]

Chromium(III) acetylacetonate (I) is much more stable. Whereas dilute mineral acids slowly attack this chelate, glacial acetic acid has no effect on this compound even at 50°. Chromium(III) acetylacetonate (I) is also stable to reduction over

(9) M. Calvin and K. W. Wilson, THIS JOURNAL, 67, 2003 (1945).
(10) R. H. Holm and F. A. Cotton, ibid., 80, 5658 (1958); this reference gives strong arguments against such aromaticity.
(11) H. G. Garg, Y. Singh and M. M. Bokadia, J. Indian Chem. Soc., 33, 353 (1956).
(12) W. J. Barry, J. Chem. Soc., 670 (1960).

Adams catalyst at 50 p.s.i. of hydrogen, and the chelate is not adsorbed on activated alumina. Such stability seems to be associated with complete saturation of the coördination sphere and coördination of the inner orbital type.

Treatment of a glacial acetic acid solution of chromium(III) acetylacetonate (I) with bromine in the presence of acetate ion afforded tris-(3-bromo-2,4-pentanediono)-chromium(III) (II) in good yield. Uptake of bromine was rapid until three moles of bromine were consumed per mole of chelate. Addition of more bromine did not result in further reaction. In the absence of acetate ion, evolution of HBr was evident and some decomposition of the chelate occurred. Cobalt(III) acetylacetonate (V) behaved in a similar manner. These and other halogenation reactions are outlined in Table I.

In order to extend the bromination reaction to chromium(III) chelates of other 1,3-diketones, tris - (1 - phenyl - 1,3 - butanediono) - chromium (III) (IX) and tris-(1,3-diphenyl-1,3-propanediono)-chromium(III) (XI) were prepared. The chelates IX and XI were synthesized by a modification of the standard preparation of chromium acetylacetonate.[13] Utilization of 96% dimethylformamide, 4% water as a solvent affords a general method for the preparation of chromium chelates of water insoluble 1,3-diketones.

Under conditions that had caused facile bromination of chromium(III) acetylacetonate (I), the chromium chelates IX and XI failed to react with bromine. Attempted brominations employing the dioxane–bromine complex and pyridine perbromide resulted in destruction of the chelates IX and XI.

N-Bromosuccinimide unexpectedly provided the best route to tris-(2-bromo-1,3-diphenyl-1,3-propanediono)-chromium(III) (XII) and tris-(2-bromo-1-phenyl-1,3-butanediono)-chromium(III) (X). In

(13) W. C. Fernelius and J. E. Blanch, Inorg. Syn., V, 130 (1957).

the absence of a radical initiator, N-bromosuccinimide in chloroform solution rapidly brominated the chelates IX and XI.

The N-halosuccinimides were found to be effective halogenating agents for all of the other acetylacetonates examined. Even the acid labile copper (II) acetylacetonate (XIII) is efficiently chlorinated by N-chlorosuccinimide. These halogenations can be carried out in glacial acetic acid or in chloroform. The latter solvent is better with acid labile chelates such as IX, XI, XIII, XV and XVII.

Iodine monochloride in glacial acetic acid buffered with acetate ion also proved to be an efficient iodinating agent of chromium(III) acetylacetonate (I) and cobalt(III) acetylacetonate (V).

The structures assigned to the halogenated chelates are based on several arguments. First, the chlorinated copper chelate XIV is identical to the chelate[14] prepared from 3-chloro-2,4-pentanedione. Thus, one halogenated chelate has been synthesized by an independent method. The structures of the other halogenated chelates are inferred by analogy.

Second, the chromium(III) chelate I reacted with one mole of bromine per chelate ring, releasing hydrogen bromide. In every instance, the elemental analyses of the halogenated products indicate one atom of halogen per chelate ring. If the methyl groups had been undergoing halogenation, more than one mole of halogen per chelate ring would have been taken up. That these methyl groups do not take part in the reaction is especially evident when one considers the bromination of the chelates IX and XI.

The infrared spectra of the halogenated chelates provide further evidence supporting the assigned structures. The spectra of the halogenated chelates are very similar, and the same pattern of changes appears when these spectra are compared to the infrared spectra of the unsubstituted chelates. All metal acetylacetonates possessing a hydrogen atom on the central carbon atom of the chelate ring exhibit two infrared bands in the 1500 to 1600 cm.$^{-1}$ region. Acetylacetonates having a group other than hydrogen at the central carbon exhibit a singlet at about 1550 cm.$^{-1}$ in their infrared spectra.[15,16] The halogenated chelates each exhibit a singlet around 1550 cm.$^{-1}$.

The upper frequency band of the doublet at 1550 cm.$^{-1}$ in the spectra of acetylacetonates has been attributed to the chelated carbonyl group; whereas, the lower band has been assigned to the partial double bonds of the chelate ring.[15] This lower frequency band is thought to disappear upon substitution of the acetylacetonate ring because of a mass effect. It seems reasonable that the doublet may arise from a coupling of the chelated carbonyl groups. The carbonyl groups in the diketo form of acetylacetone give rise to two carbonyl stretching bands—a result that can only arise from coupling.[14]

(14) H. F. Holtzclaw, Jr., and J. P. Collman, THIS JOURNAL, **79**, 3318 (1957).

(15) R. P. Dryden and A. Winston, *J. Phys. Chem.*, **62**, 635 (1958).

(16) For a review of the infrared spectra of metal acetylacetonates see F. A. Cotton in "Modern Coördination Chemistry," edited by J. Lewis and R. G. Wilkins, Interscience Publishers, Inc., New York, N. Y., 1960, p. 379.

The ultraviolet spectra[17] of the halogenated chelates and the unsubstituted chelates are listed in Table II. Comparison of the spectrum of each unsubstituted chelate with that of the corresponding halogenated chelate clearly illustrates an extension of conjugation. Only introduction of halogen at the central carbon of the chelate ring would produce this spectral shift to longer wave lengths.

TABLE II

ULTRAVIOLET DATA FOR CHELATES[a]

Compound	λ max., mμ	ε (l./mole-cm.)
[HCAc$_2$]$_3$Cr	335	15,800
[ClCAc$_2$]$_3$Cr	357	11,700
[BrCAc$_2$]$_3$Cr	358	13,070
[ICAc$_2$]$_3$Cr	362	11,900
[HCAc$_2$]$_3$Co	258[b]	38,800[b]
[ClCAc$_2$]$_3$Co	258	25,800
	343	6,900
[BrCAc$_2$]$_3$Co	261	27,700
	343	7,760
[ICAc$_2$]$_3$Co	275	43,800
[HCAc$_2$]$_3$Al	286	42,900
[BrCAc$_2$]$_3$Al	310	36,800
[HCBzAc]$_3$Cr[c]	358	24,050
[BrCBzAc]$_3$Cr	373	16,750
[HCBz$_2$]$_3$Cr	385	33,300
[BrCBz$_2$]$_3$Cr	392	20,300

[a] These spectra were measured at about 10^{-5} M in chloroform. [b] These values were taken from ref. 10. [c] Bz represents benzoyl.

A number of attempts to carry out reactions on tris - (3 - bromo - 2,4 - pentanediono) - chromium (III) (II) have failed, but the results are interesting inasmuch as they reflect on the chemical nature of the bromine atoms on the chelate ring. The analogous iodo chelate behaved in a similar manner.

Treatment of the brominated chromium chelate II with magnesium or lithium in tetrahydrofuran, benzene or ether failed to initiate any reaction even after extended periods at the boiling points of these solvents. In each case, the starting material was recovered.

Nucleophilic displacements of the bromine from the brominated chelate II by azide, acetate, nitrite and iodide ions failed in hot (100°) dimethylformamide. In each instance the chelate II was recovered unchanged. Sodium ethoxide in cold ethanol and zinc powder in boiling ethanol caused decomposition of the brominated chelate II.

The mechanism of chelate halogenation will be the subject of a future publication. It should suffice here to state that the chelate molecule must exhibit a high electron density at the central carbon atom. Whether or not this occurs through partial ionization and ring opening is an interesting question fundamental to all reactions of chelates of 1,3-diketones. An obvious extension of these halogenation studies is the investigation of reactions such as nitration, mercuration and the Friedel–Crafts processes. Preliminary investigations of these reactions are currently being carried out in this Laboratory.

(17) For a review of the ultraviolet spectra of metal acetylacetonates see ref. 10.

Experimental[18,19]

Tris-(3-bromo-2,4-pentanediono)-chromium(III) (II).— (A) A solution of bromine (12.1 g., 0.076 mole) in 20 ml. of acetic acid was added slowly, with stirring, to a solution of tris-(2,4-pentanediono)-chromium(III) (I) (6 g., 0.017 mole) and potassium acetate (5.1 g., 0.052 mole) in 150 ml. of acetic acid at 30°. After five minutes the precipitate was collected, washed with water, sodium bicarbonate solution, sodium bisulfite solution and again with water. The brown substance was recrystallized from benzene–heptane. The yield of brown crystals was 6.5 g. (64%), m.p. 228–229°.

Anal. Calcd. for $C_{15}H_{18}CrO_6Br_3$: C, 30.74; H, 3.10; Br, 40.91. Found: C, 30.95; H, 3.35; Br, 40.72.

(B) A solution of N-bromosuccinimide (0.4 g., 0.023 mole) in 10 ml. of acetic acid was added slowly, with stirring, to a solution of tris-(2,4-pentanediono)-chromium(III) (I) (0.5 g., 0.0014 mole) in 10 ml. of acetic acid at room temperature. After five minutes the precipitate was collected, washed as in part A and recrystallized from benzene–heptane. The yield of brown crystals was 0.5 g., (60%), m.p. 226–228°.

Tris-(1,3-diphenyl-1,3-propanediono)-chromium(III) (XI). —Chromium(III) chloride-6-hydrate (7 g., 0.027 mole),1, 3-diphenyl-1,3-propanedione (18 g., 0.080 mole) and urea (25 g.) were dissolved in 200 ml. of 96% dimethylformamide, 4% water at 100°. The solution was maintained at 100–120° for 24 hr., poured over ice and diluted with water (total volume 300 ml.). The green precipitate was collected, washed with water and recrystallized from benzene–heptane. The yield of brown crystals was 10.5 g. (65%). An analytical sample recrystallized four times from benzene–heptane melted at 317–318°. The infrared spectrum of this compound (CHCl₃) exhibits an intense doublet at 1520–1535 cm.⁻¹.

Anal. Calcd. for $C_{45}H_{33}CrO_6$: C, 74.90; H, 4.58. Found: C, 75.07; H, 4.47.

Tris-(1-phenyl-1,3-butanediono)-chromium(III) (IX).— Chromium(III) chloride-6-hydrate (4 g., 0.015 mole), 1-phenyl-1,3-butanedione (13 g., 0.080 mole) and urea (25 g.) were dissolved in 125 ml. of 96% dimethylformamide at 100°. The solution was maintained at 100–120° for 24 hr., poured over ice and diluted with water (total 300 ml.). The green precipitate was collected and recrystallized from benzene–heptane. The yield of olive-drab crystals was 4 g. (50%). An analytical sample recrystallized four times from benzene–heptane melted at 237–238°. The infrared spectrum (CHCl₃) of this compound exhibits intense chelated carbonyl bands at 1545 and 1510 cm.⁻¹, and two bands of lesser intensity at 1580 and 1490 cm.⁻¹, probably due to the phenyl groups.

Anal. Calcd. for $C_{40}H_{27}CrO_6$: C, 67.28; H, 5.08. Found: C, 67.23; H, 5.38.

Tris-(2-bromo-1,3-diphenylpropanediono)-chromium(III) (XII).— A mixture of N-bromosuccinimide (4 g., 0.023 mole) and tris-(1,3-diphenylpropanediono)-chromium(III) (XI) (4 g., 0.0055 mole) in 140 ml. of chloroform was boiled for five minutes, washed with aqueous sodium bisulfite and then washed with water. The chloroform solution was dried, the chloroform was removed and the resulting solid recrystallized from benzene–heptane. The yield of brown crystals was 4 g. (65%). An analytical sample, recrystallized four times from benzene–heptane melted at 254–258°.

(18) All melting points were determined on the Kofler micro hot stage melting point apparatus. All infrared spectra were measured on a Perkin–Elmer Infracord. All ultraviolet spectra were measured on a recording Cary Spectrophotometer by T. D. Epley. Analyses were performed by Micro-Tech Laboratory, Skokie, Illinois, by G. Weiler and F. B. Strauss, Microanalytical Laboratory, Oxford, England, by Schwarzkopf Microanalytical Laboratory, Woodside, New York, and by K. L. Shepard of the University of North Carolina.

(19) Only representative examples of each type of halogenation experiment are listed. The procedures are completely analogous in each other case.

Anal. Calcd. for $C_{45}H_{30}CrO_6Br_3$: C, 56.37; H, 3.13; Br, 25.05. Found: C, 56.89; H, 3.51; Br, 24.75.

Tris-(3-iodo-2,4-pentanediono)-chromium(III) (III).— (A) A solution of iodine monochloride (4.5 g., 0.028 mole) in 20 ml. of acetic acid was added slowly with stirring to a solution of tris-(2,4-pentanediono)-chromium(III) (I) (3 g., 0.0086 mole) and potassium acetate (2.5 g., 0.025 mole) in 70 ml. of acetic acid at 35°. After five minutes the precipitate was collected, washed with water, sodium bicarbonate solution, sodium bisulfite solution and again with water. The brown solid was recrystallized from benzene–heptane yielding 4.5 g. (72%) of black crystals, m.p. 224–225°.

Anal. Calcd. for $C_{15}H_{18}CrO_6I_3$: C, 24.77; H, 2.50; I, 52.37. Found: C, 24.18; H, 2.72; I, 51.65.

(B)—The iodo chromium chelate(III) was prepared from N-iodosuccinimide in glacial acetic acid in the usual manner. This product, obtained in 62% yield, was identical to the iodo chelate prepared by method A.

Tris-(3-chloro-2,4-pentanediono)-chromium(III) (IV).— This substance was prepared from N-chlorosuccinimide in the usual manner—65% yield. The light green powder melted at 205°.

Anal. Calcd. for $C_{15}H_{18}CrO_6Cl_3$: C, 39.80; H, 4.01. Found: C, 40.11; H, 4.23.

Tris-(3-bromo-2,4-pentanediono)-cobalt(III) (VI).— This substance was prepared from bromine in buffered acetic acid (53%) and from N-bromosuccinimide in chloroform (84%). The black crystals melted at 232–233°.

Anal. Calcd. for $C_{15}H_{18}CoO_6Br_3$: C, 30.38; H, 3.06; Br, 40.43. Found: C, 30.83; H, 3.13; Br, 40.11.

Tris-(3-iodo-2,4-pentanediono)-cobalt(III) (VII).—This substance was prepared from iodine monochloride in buffered acetic acid (97%) and from N-iodosuccinimide in chloroform (42%). The black crystals obtained from recrystallization of the green powder melted at 160–162°.

Anal. Calcd. for $C_{15}H_{18}CoO_6I_3$: C, 24.55; H, 2.47; I, 51.87. Found: C, 25.27; H, 2.65; I, 51.71.

Bis-(3-chloro-2,4-pentanediono)-copper(II) (XIV).—This substance was prepared from N-chlorosuccinimide in chloroform (78%). The halogenated chelate XIV precipitated from the chloroform solution. The green needles had the same infrared spectrum as an authentic sample[14] of the chelate XIV.

Tris-(3-bromo-2,4-pentanediono)-aluminum(III) (XVI).— This substance was prepared from N-bromosuccinimide in chloroform (58%). The brominated aluminum chelate was a white powder, m.p. 215–216°.

Anal. Calcd. for $C_{15}H_{18}AlO_6Br_3$: C, 32.11; H, 3.23; Br, 42.73. Found: C, 32.30; H, 3.40; Br, 43.00.

Tris-(3-bromo-2,4-pentanediono)-iron(III) (XVIII).— This substance was prepared from N-bromosuccinimide in chloroform. The deep red crystals (55%) were very soluble in all organic solvents. Recrystallization from heptane afforded an analytical sample, m.p. 170°. The solid is not stable and slowly evolves a lachrymatory substance.

Anal. Calcd. for $C_{15}H_{18}FeO_6Br_3$: C, 30.54; H, 3.08; Br, 40.64. Found: C, 32.28, 32.57; H, 3.43, 3.38; Br, 41.15, 41.16.

Attempted Elaborations of Tris-(3-bromo-2,4-pentanediono)-chromium(III) (II).—The bromo chelate II was treated in separate experiments with potassium iodide, sodium nitrite, sodium azide and potassium acetate in dimethylformamide at 100° for 12 hr. Starting material was recovered in high yield from each attempted reaction. Aluminum chloride in chloroform, sodium ethoxide in cold ethanol and zinc dust in boiling ethanol each caused the destruction of the bromo chelate II.

Treatment of the chelate II with lithium or magnesium chips in boiling tetrahydrofuran, ether or benzene for extended periods did not result in any reaction. Each of these attempts was carried out under a nitrogen atmosphere. Starting material was recovered each time.