placed beyond the end of the spectrum, *i.e.* below 650 cm.$^{-1}$.) Pyridine has a strong band at 670 cm.$^{-1}$ which has been assigned to a hydrogen out-of-plane vibration[8]; however, it is not immediately apparent why such a vibration should be sensitive to the type of chelate compound. It can be shown with models that in the case of the octahedral complexes with a bridged structure the three pyridine rings attached to each metal ion occupy a face of the octahedron, whereas in the tridentate two-to-one compounds, even though there are more pyridine groups per metal ion, there is less crowding. Thus, steric factors may be significant. However, no explanation can be given for the shift in this band for $Cu_2(PAA)Cl_4$, which should have the least steric hindrance of any of the compounds. This suggests that the effect may, in fact, be electronic rather than steric.

TABLE III

LOW FREQUENCY INFRARED ABSORPTION BAND

Pyridinaldazine	685 s
Tridentate compounds	
$Fe(PAA)_2^{+2}$	664 m
$Co(PAA)_2^{+2}$	658 m
$Ni(PAA)_2^{+2}$	665 m
$Cu(PAA)Cl^{+}$	664 m
Bridged compounds	
$Fe_2(PAA)_3^{+4}$	...
$Co_2(PAA)_3^{+4}$	...
$Ni_2(PAA)_3^{+4}$	...
$Cu_2(PAA)Cl_4$	...

To summarize: both the C=N band and high frequency pyridine ring vibration in pyridinaldazine have been shown to be sensitive to the structure of the chelate compound. In both cases the changes have been interpreted to be entirely consistent with the proposed structures for the two types of complexes. One additional band, from hydrogen out-of-plane vibration on the pyridine rings, also has been shown to be structurally sensitive to the type of complex, but no conclusive explanation can be given at this time. Although these observations do not in themelves prove the postulated structures, nevertheless they do contribute significantly to the total structural information about these very interesting and unusual compounds.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF UNION CARBIDE PLASTICS COMPANY, BOUND BROOK, NEW JERSEY]

Inner Complexes. III. Ring Bromination of β-Dicarbonyl Chelates

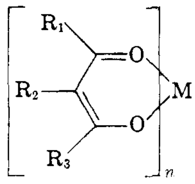
BY RUDOLPH W. KLUIBER

RECEIVED MARCH 18, 1960

N-Bromosuccinimide is a general reagent for replacing the ring hydrogen of metal β-dicarbonyl chelates with bromine. Tracer studies indicate that this substitution can occur without any intermediate ring cleavage.

Inner complexes frequently possess physical properties such as solubility, melting point and hydrolytic stability characteristic of organic compounds rather than inorganic salts.[1,2] This analogy is extended by the reported reactivity of metal chelates having pendant functional groups in characteristic organic reactions involving these groups, wherein the chelate ring remains intact.[3-6] Less common, however, are substitution reactions on the ring itself in which the reaction proceeds without apparent cleavage of the chelate ring.

Considering specifically the metal β-dicarbonyl compounds (A), most reported reactions with reagents such as bromine,[7] acetyl chloride[8] and sulfur chloride,[9] lead to products of ring cleavage. As an exception, the bromination of chromium(III) tris-(2,4-pentanedionate) with elemental bromine produces the tribromide A($M = Cr$, $R_1 = R_3 = CH_3$, $R_2 = Br$, $n = 3$).[10] Nitrogen tetroxide and



(A)

copper bis-(2,4-pentanedionate) are reported to form the dinitro derivative A ($M = Cu$, $R_1 = R_3 = CH_3$, $R_2 = NO_2$, $n = 2$).[11] Kinetic data also support the formation of the brominated intermediate A ($M = Cu$, $R_1 = CH_3$, $R_2 = Br$, $R_3 = OC_2H_5$, $n = 2$) in the cupric ion catalyzed bromination of ethyl 3-ketobutyrate.[12] None of these reactions appears to be generally applicable to metal β-dicarbonyl chelates, nor has any conclusive evidence been published to demonstrate that substitution occurs directly on the chelate ring rather than through ring cleavage with subsequent reformation of the ring.

It has now been found that N-bromosuccinimide reacts with stoichiometric amounts of metal β-dicarbonyl chelates A ($R_2 = H$) to form ring brominated derivatives A ($R_2 = Br$). The success

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[3] A. C. Kurtz, *J. Biol. Chem.*, **180**, 1253 (1949).

[4] (a) P. Pfeiffer, W. Offerman and H. Werner, *J. prakt. Chem.*, **159**, 313 (1942); (b) H. S. Verter and A. E. Frost, THIS JOURNAL, **82**, 85 (1960).

[5] J. C. Bailar, WADC TR 57-657, p. 35.

[6] See also last example in Experimental part of this article.

[7] K. V. Auwers and E. Auffenbery, *Ber.*, **50**, 29 (1917).

[8] A. Michael and G. H. Carlson, THIS JOURNAL, **58**, 353 (1936).

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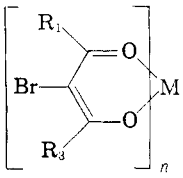
TABLE I

CHARACTERIZATION OF



					Re-crystalliz.[a]	Calcd., %			Found, %		
R_1	R_3	M	n	M.p., °C.	solvent	C	H	Br	C	H	Br
Me	Me	Al III	3	215.5–216	1	32.1	3.2	42.7	32.5	3.8	42.0
Me[b]	Me	Al III	3	215.5–216	2	28.2	2.8	70.5[c]	28.4	2.6	69.8[c]
Me	OEt	Al III	3	132–134	3	33.2	3.7	36.8	33.2	3.9	..
Me	Me	Be II	2	177–179	1	32.9	3.3	43.8	32.8	2.9	43.5
Me	Me	Co III	3	170 dec.	1	36.5	3.7	40.4	..	..	42.0
Me[b]	Me	Co III	3	170 dec.	2	27.0	2.7	33.6	27.5	2.8	..
Me	Me	Cr III	3	240–241	1	30.7	3.1	40.9	30.4	2.9	41.2
Me[b]	Me	Cr III	3	240–241	2	27.2	2.7	34.0	27.5	2.8	34.1
Me	Me	Cu II	2	Dec. <200	4	28.6	2.9	38.1	..	..	38.1
Me	Ph	Cu II	2	208–210	5	44.5	2.9	29.2	44.5	2.7	29.3
Me	Me	Fe III	3	201–203	1	30.5	3.1	40.6	30.8	2.7	..
Me	Me	Ga III	3	212–212.5	1	29.8	3.0	39.7	30.7	3.2	..
Me	Me	Sc III	3	180 dec.	1	31.1	3.1	41.4	32.1	3.5	..
Me	Me	VO II	2	Dec. <200	6	28.4	2.9	37.8	28.9	2.6	..

[a] Recrystallization solvents: 1, benzene petroleum ether; 2, benzene–chloroform; 3, sublimation; 4, benzene; 5, N,N-dimethylformamide; 6, toluene. [b] Chloroform clathrates. [c] Contained chlorine calculated as bromine.

of this bromination appears due mainly to the absence of reactive or strongly acidic by-products. A list of compounds prepared is given in Table I. In addition, the bromination was successfully applied to imine-containing chelates. The Experimental section describes the bromination of the nickel chelate of N-*n*-butylsalicylimine and the copper chelate of bis-(2,4-pentanedione)-ethylene diimine.

The structure of these bromo chelates was confirmed by elemental analysis and in the case of copper bis-(3-bromo-2,4-pentanedionate) by comparison with an authentic specimen.[13] The infrared spectra of the bromo chelates from 2,4-pentanedione contained only a single strong absorption peak in the 6.25–6.75 μ region[14] and no peak in the 8.3 μ area[11] in agreement with the assigned structure.

The tris-(3-bromo-2,4-pentanedionates) of aluminum(III), chromium(III) and cobalt(III) form chloroform adducts which probably are clathrates. Previous workers[15] have reported the formation of chloroform-bearing chelates of the 2,4-pentanedionates of aluminum(III), chromium(III) and iron (III) containing two chloroform molecules per chelate. These materials were very soluble in an excess of chloroform and lost solvent upon standing in air. In contrast, the clathrates of the bromo chelates form 1:1 chloroform–chelate ratios are rather insoluble in an excess of chloroform and are stable up to temperatures as high as 60–80° and even higher in the case of cobalt(III). The structures of these clathrates was confirmed by analytical data and the presence in the infrared spectra of a strong absorption at 13.25 characteristic of chloroform. Desolvation was accomplished by heating *in vacuo* at temperatures above 100°. In the absence of any X-ray data, the exact structure of these clathrates cannot be demonstrated, but their stability is influenced by steric effects. Thus the corresponding 3-chloro chelates do not form such clathrates, whereas the 3-iodo chelates do.[16] Also 1:1 clathrates are formed with methylene chloride but not with carbon tetrachloride.[16]

A compound previously reported by Reihlen, Illig and Wittig[10] to be the hexabromide A (M = Cr, R_1 = CH_2Br, R_2 = Br, R_3 = CH_3, n = 3) now has been shown to be identical to the 1:1 chloroform clathrate by direct comparison. The clathrate structure is in agreement with the published analytical data and explains the poor yields reported.

Experimental

General Procedure for Bromination of Metal β-Dicarbonyl Chelates.—To 20 meq. of the metal β-dicarbonyl chelate (samples of chelates obtained from Union Carbide Metals Co.) in 25 ml. of chloroform is added with stirring 22 meq. of powdered N-bromosuccinimide. After five minutes, the reaction mixture is heated and concentrated to 10 ml. in a stream of nitrogen. Approximately 50–100 ml. of petroleum ether is added and the precipitated mass collected, dried and sublimed at 125° (0.1 mm.) to remove succinimide. The residue is recrystallized from an appropriate solvent to yield the pure bromochelate in yields of 50–90%. An alternate work-up procedure for Al (III), Cr(III) or Co(III) 2,4-pentanedionates involves addition of chloroform, approximately 25 ml., to dissolve the succinimide and collecting the bromo chelate as its insoluble clathrate. The succinimide can also be removed from the crude mixture containing chromium(III) tris-(3-bromo-2,4-pentanedionate) by washing it with 10% sodium hydroxide solution. The use of carbon tetrachloride as reaction solvent gives slower reaction, but the succinimide can be removed directly by filtration and quite pure bromide precipitated from a solution by addition of petroleum ether. A list of bromo chelates appears in Table I.

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(16) R. W. Kluiber, unpublished data.

Bromination of Copper(II) Ethylene Diamine-bis-2,4-Pentanedione.—One gram (6.9 meq.) of copper II ethylene diamine-bis-2,4-pentanedione and 1.25 g. (7.0 meq.) of N-bromosuccinimide were dissolved in 25 ml. of chloroform and the reaction mixture precipitated after 30 minutes by addition of petroleum ether. The dried solid was sublimed at 100° (0.1 m.) for 48 hr. and the residue recrystallized several times from benzene petroleum ether to give a small amount of silver violet crystals, m.p. dec. 135°.

Anal. Calcd. for $C_{12}H_{16}O_2N_2Br_2Cu$: C, 32.5; H, 3.6. Found: C, 32.9; H, 4.2.

Bromination of the Ni(II) Chelate of N-*n*-Butylsalicylimine.—To 25 ml. of chloroform was added 4.1 g. (20.0 meq.) of nickel bis-N-*n*-butylsalicylimine and 3.5 g. (19.6 meq.) of N-bromosuccinimide. After 30 minutes most of the succinimide was removed by careful precipitation with petroleum ether. The dibromide was recovered by precipitation with additional petroleum ether in essentially quantitative yield. After several recrystallizations from chloroform–petroleum ether and benzene–petroleum ether, it had a melting point of 193–194°.

Anal. Calcd. for $C_{22}H_{26}O_2N_2Br_2Ni$: C, 46.4; H, 4.6; N, 4.9; Br, 28.1. Found: C, 46.0; H, 4.9; N, 5.3; Br, 28.7.

Preparation of "Hexabromo" Chromium(III) Tris-(2,4-pentanedionate).[10]—To a solution of 1.75 g. (15.1 meq.) of chromium(III) tris-(2,4-pentanedionate) in 50 ml. of chloroform was added 3 g. (18.7 meq.) in 20 ml. of chloroform. The reaction mixture was allowed to stand for 15 minutes. Petroleum ether, 100 ml., was added to precipitate 2.5 g. of product (reported yield 2.5 g.). Recrystallization from benzene–chloroform gave 1.9 g., m.p. 240°. Both the crude and purified products gave infrared spectra identical with chromium(III) tris-(3-bromo-2,4-pentanedionate) 1:1 chloroform clathrate.

Anal. Calcd. for $C_{16}H_{19}O_6Br_3Cl_3Cr$: halogen (calculated as gravimetrically determined Br), 59.5; Cr, 7.4. Calcd. for $C_{15}H_{15}O_6Br_6Cr$: Br, 58.2; Cr, 6.3. Found: Br, 59.2; Cr, 6.5.

Competitive Reactions.—The studies (a, b, c) were carried out in support of the competitive bromination (d).

(a) 2,4-Pentanedione 1.00 g. (10.0 meq.) and 1.78 g. of N-bromo-succinimide were added to 10 ml. of chloroform with stirring. After 5 minutes 1.16 g. (10.0 meq.) of chromium(III) tris-(2,4-pentanedionate) was added and the solution stirred for 20 minutes, concentrated *in vacuo* and petroleum ether added to yield 1.925 g. of solid. Sublimation of 1.000 g. of this solid yielded 0.510 g. (85% recovery) of starting chromium(III) tris-(2,4-pentanedionate), m.p. 217–219°. 3-Bromo-2,4-pentanedione was recovered as the petroleum ether solution and reaction of the concentrates with copper acetate. This experiment indicates that no exchange between chromium tris-(2,4-pentanedionate) and 3-bromo-2,4-pentanedione occurs under these conditions.

(b) Chromium(III) tris-(3-bromo-2,4-pentanedionate), 1.95 g. (10.00 meq). and 1.00 g. of pentane-2,4-dione were dissolved in 10 ml. of benzene. After 0.5 hr. precipitation with petroleum ether produced only unchanged chromium (III) tris-(3-bromo-2,4-pentanedionate), m.p. 235–237°. Again no exchange takes place.

(c) N-Bromosuccinimide, 1.78 g. (approx. 10.0 meq.) was added to a solution of 1.160 g. (10.0 meq.) of chromium (III) tris-(2,4-pentanedionate) in 10 ml. of chloroform. After 30 minutes the reaction was worked up as in part a, yielding 3.170 g. of crude product, 1.0 g. of which yielded upon sublimation 0.544 g., 90% recovery of material containing 38.9% bromine. This corresponds to a 93.3% purity of the N-bromosuccinimide used.

(d) To a mixture of 1.00 g. (10.0 meq.) of 2,4-pentanedione and 1.16 g. (10.0 meq.) of chromium(III) tris-(2,4-pentanedionate) was added 1.78 g. of N-bromosuccinimide. After 10 minutes the reaction was worked up as in part a, yielding 2.60 g. One gram of this gave after sublimation a residue of 0.507 g. (83% recovery) of product containing 25.8% bromine. This corresponds to 54.6% of the available bromine entering the chelate.

Exchange Reactions Using C_{14} Labelled 2,4-Pentanedione.—Tracer studies were carried out using 2,4-pentanedione-1,3-C^{14}. Counting was carried out using standard weights of active materials in a standard cup. Standards were prepared in order to determine per cent. exchange.

(a) C_{14} labelled 2,4-pentanedione (1 g. (10 meq.)) and metal 2,4-pentanedionate were dissolved in 10 ml. of chloroform. After ten minutes the chelate was precipitated with petroleum ether, removed by filtration, carefully washed and dried. The per cent. exchange found for the metal 2,4-pentanedionates under these conditions was Sc(III), VO (II), Mn(III), Cu(II), Ga(III), 100%; Fe(III), 90%, Ni(II) 70%; Be(II), 30%; Al(III), 20%; Cr(III), 1%; and Co(III), 0%.

(b) A parallel series was run using 1 g. of labelled 2,4-pentanedione, 1 g. of metal 2,4-pentanedionate and 20 ml. of dioxane Mg(II) and Cu(II), 100%; Fe(III), 50%; Al (III), 3%. The copper (II) and magnesium(II) derivatives were not completely soluble but exchange was complete regardless.

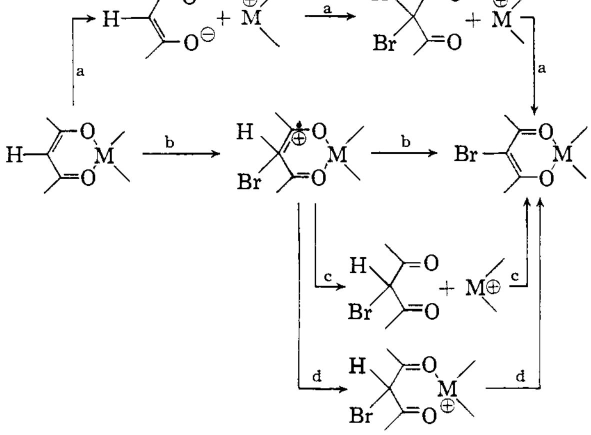
(c) To a solution containing 10 meq. of metal 2,4-pentanedionate and 10 meq. of 2,4-pentanedione in 10 ml. of chloroform was added 20 meq. of N-bromosuccinimide. After 10 minutes, the product was isolated, purified and counted. The per cent. exchange decreased in the order Cu(II), 100%; Be(II), 10%; Al(III), 3%; Cr(III), <1%. The amount of exchange occurring was either equal to the amount of exchange anticipated without reaction (part a) or less.

Acetylation of Copper(II) Bis-N-2-hydroxyethylsalicylimine.—To a suspension of 10 g. (0.12 mole) of sodium bicarbonate and 15 g. (0.028 mole) of copper(II) bis(N-2-hydroxyethylsalicylimine) in 100 ml. of chloroform was added with vigorous stirring 10 g. (0.01 mole) of acetic anhydride over a period of 30 minutes. The suspension was stirred 2.5 hr. filtered and the copper chelate isolated by concentration of the chloroform solution and addition of petroleum ether to yield 17 g. (95%), m.p. 146–151°.

Anal. Calcd. for $C_{12}H_{24}O_6N_2Cu$: C, 55.52; H, 5.08; N, 5.88. Found: C, 55.29; H, 4.90; N, 5.85.

TABLE II

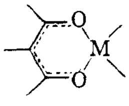
BROMINATION ROUTES

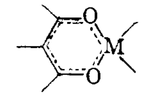


Discussion

Reaction of metal bis-β-dicarbonyls with N-bromosuccinimide to produce bromo chelates can be visualized as proceeding by several routes (Table II). As examples bromination may proceed through initial ring cleavage and then halogenation and ring formation (a, Table II). Or halogenation of the ring itself could give rise to an intermediate which stabilizes itself by partial or complete ring cleavage (c and d, Table II). Finally, bromination may take place with the ring remaining intact throughout the transformation (b, Table II). In this later reaction, the metal chelate acts chemically similar to a metal containing heterocycle or a *metalloheterocycle*. Initial side chain halogenation followed by rearrangement of the halogen to the ring is ruled out by the apparent stability of the known halomethyl chelates A (R_1, R_3 = CH_2Br, CH_2I).

It is anticipated that should any ring cleavage occur in a reaction carried out in the presence of excess β-dicarbonyl compound, exchange should occur. Using C^{14} labelled 2,4-pentanedione and metal 2,4-pentanedionates in approximately equivalent amounts and adding enough N-bromosuccinimide to monobrominate both diketone and chelate, it was found that the exchange which occurred was less than or at most equal to the exchange which occurs in the absence of N-bromosuccinimide. It was shown thus that the reaction of N-bromosuccinimide in chloroform with the 2,4-pentanedionates of beryllium(II), aluminum(III) and chromium(III) proceeds essentially without additional exchange. However, in addition to route b (Table II) it is possible to obtain the same results by routes such as c (Table II) if it is assumed that halogenation of the chelate ring occurs very much faster than halogenation of the diketone and that the intermediate chromium complex formed by ring cleavage combines much more rapidly with the bromo diketone than the diketone. To eliminate this possibility, a competitive bromination was carried out in which essentially 1 equivalent each of 2,4-pentanedione and chromium(III) tris-(2,4-pentanedionate) were allowed to react with only one equivalent of N-bromosuccinimide. Approximately 55% of the available bromine appeared in the chelate indicating that the reaction rates are quite comparable. Thus, the bromination of chromium(III) tris-(2,4-pentanedionate) proceeds without any intermediate ring cleavage. Presumably, the other chelates react similarly.


B


C

The structure of β-dicarbonyl compounds has been assumed generally to be either the resonance stabilized form B or the aromatic system[17] C. Evidence for the aromaticity of β-dicarbonyl chelates stems principally from the extraordinary stability, hydrolytic and/or thermal, of some of the members.[18,19] Yet attempts to demonstrate this aromaticity conclusively have failed.[17,20] Aromatization of these chelate rings would require the donation of non-bonding *p*-electrons on coördinated oxygen atoms to 3d, 4p, or 4d orbitals on the metal. Such an electron shift does not appear too probable in view of the formal negative charge already on the metal atom. The consequence of this electron shift toward the metal would be a decrease in electron charge on the remainder of the ring and a reduced tendency toward electrophilic substitution. This is not observed in the competition for bromine between equivalent quantities of 2,4-pentanedione and chromium(III) tris-(2,4-pentanedionate). In chloroform it has been estimated that 2,4-pentanedione exists as approximately 90% enol.[21] If it assumed that the chromium chelate is 100% enolic, it would account for 53% of the enol in the system. The actual isolation of 55% of the bromine on the chelate is within experimental error and suggests that, assuming electrophilic substitution, little if any aromatic character exists. Likewise, the rate of exchange between 2,4-pentanedione and its metal chelates can be rationalized on the basis of charge/radius ratios[22] and the availability of empty orbitals on the metal[23] and does not support any appreciable aromatic character.

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[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES OF BROWN UNIVERSITY, PROVIDENCE, RHODE ISLAND]

Ethane 1,2-Diamineborane

BY HENRY C. KELLY AND JOHN O. EDWARDS

RECEIVED FEBRUARY 22, 1960

Ethylenediamine absorbs diborane in a 1:1 mole ratio to form a compound of empirical formula $(CH_2NH_2BH_3)_2$, named ethane 1,2-diamineborane. Preparation has been carried out by heterogeneous absorption of diborane by ethylenediamine in the high vacuum apparatus and by reaction of ethylenediamine with the tetrahydrofuran-borane complex. Chemical composition has been verified by molar ratio of reactants and chemical analysis. The compound, a white crystalline solid, is stable in air and undergoes decomposition when heated to 89°. On prolonged heating *in vacuo* at 90–110°, two moles of hydrogen are liberated per mole starting material. Ethane, 1,2-diamineborane is a highly selective reducing agent exhibiting a reactivity comparable to sodium borohydride. Reactions with various organic and inorganic reagents, solubility characteristics and possible structural assignments are discussed.

Introduction

Nitrogen derivatives of the boron hydrides have been known for a considerable length of time. Early work in this field is described by Stock,[1] who with co-workers prepared and studied various properties of the diammoniate of diborane.[2-5]

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[3] A. Stock and E. Pohland, *ibid.*, **58**, 657 (1925).

[4] A. Stock and E. Pohland, *ibid.*, **59**, 2210 (1926).

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