Reactions of Metal Chelates. VI.[1,2] The Synthesis and Reactions of a Stable Chelate Diazonium Salt[3]

JAMES P. COLLMAN AND MICHIHIRO YAMADA[4]

Venable Laboratory, Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina

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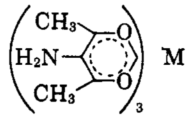
A monoamine derivative L of chromium(III) acetylacetonate has been prepared by reduction of a mononitro derivative I. The chelate amine L was transformed into a stable chelate diazonium fluoroborate N. The diazonium salt was converted into a monofluoro chelate O. Nitration of mono- and dichloro chromium acetylacetonates afforded a series of chloro-, nitro-substituted chelates. Apparent displacement of chloro by nitro was observed during nitration of the dichloro chelate C.

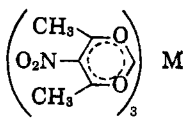
Recent reports from this and other laboratories have described the quasiaromatic properties of metal complexes of acetylacetone.[1,5–13] These chelates undergo a wide variety of electrophilic substitution reactions under relatively mild conditions. Stereochemical studies indicate that these substitutions are not attended by opening of the chelate rings.[14,15] The proton magnetic resonance spectra of unsymmetrically substituted metal acetylacetonates[7] and of certain acetylacetone–ethylene diamine complexes[16] suggest the presence of aromatic ring current in these substances. Classically, one of the most significant chemical indications of aromatic character is the stabilization of a diazonium ion. This paper reports a successful preparation of a chelate diazonium salt and its chemical properties.

Our first attempts to synthesize amino-substituted metal acetylacetonates A, the logical precursors of chelate diazonium salts, were unsuccessful. Attempts at direct amination of the chelate ring failed. Nitro-substituted chelates B, available from a previous study,[5] seemed to offer a route to the desired amino chelates A.

However, all attempts to reduce nitro groups on the nitrocobalt(III) or rhodium(III) chelates led to reduction of the metals and subsequent decomposition of the complexes.[5] On the other hand, chemical or catalytic reductions of the nitro chromium chelate B either afforded unchanged starting material or resulted in intractable mixtures of unidentified products. We had previously experienced difficulty in carrying out transformations on other trifunctional chelates.[11] It soon became apparent that the reduction of a trinitro chelate would be a formidable task. Our goal then became the synthesis of a chromium(III) chelate containing a single nitro group.



A



B

M = Cr, Co, Rh

At this time we had prepared dichloro chromium acetylacetonate (C) for another study.[7] It appeared that this dichloro chelate C easily could be transformed into the dichloromononitro chelate D which could then be reduced to a monoamino chelate—avoiding the difficulties of reducing a trinitro derivative. Chloro groups on these chelate rings were known to be resistant to catalytic reduction.

Preliminary experiments revealed that the trichloro chelate E was inert under the conditions of nitration. This, of course, was to be expected. However, nitration of the dichloro compound C with copper nitrate trihydrate in acetic anhydride afforded a mixture of three chelates. These were separated by chromatography and eventually characterized as the expected dichloro mononitro chelate D and, unexpectedly, the dinitro monochloro chelate F, and the trichloro chelate E (Chart I). These surprising results may be interpreted in two ways: (a) disproportionation of the acetylacetonate rings during the reaction or (b) electrophilic cleavage of chlorine by the nitrating agent, followed by subsequent chlorination of the starting material in the presence of the released positive halogen.

The first of these alternative explanations is less likely in view of the retention of optical activity during electrophilic substitution of these chelate rings.[14,15] However, it is evident that this nitration should be carried out on the resolved dichloro chromium acetylacetonate C in order to reaffirm the validity of this assumption. The concept of electrophilic cleavage of halogen from these chelate rings by the nitrating reagent seems more plausible in view of our earlier experience with electrophilic substitutions[17] of groups other than hydrogen from metal acetylacetonate rings. Indeed, in all of the cases that we have examined,[11,17] disubstituted trisacetylacetonates undergo these cleavage reactions at a much greater rate than the mono- or the trisubstituted compounds. In order to investigate

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[3] Supported by research Grant DA-ARO-(D)-31-124-G185, U. S. Army Research Office, Durham, N. C.

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[5] J. P. Collman, R. L. Marshall, W. L. Young, III, and S. D. Goldby, *Inorg. Chem.*, **1**, 704 (1962).

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[13] R. W. Kluiber, *ibid.*, **83**, 3030 (1961).

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[15] J. P. Collman, R. P. Blair, R. L. Marshall, and L. Slade, *Inorg. Chem.*, **2**, 576 (1963).

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CHART I

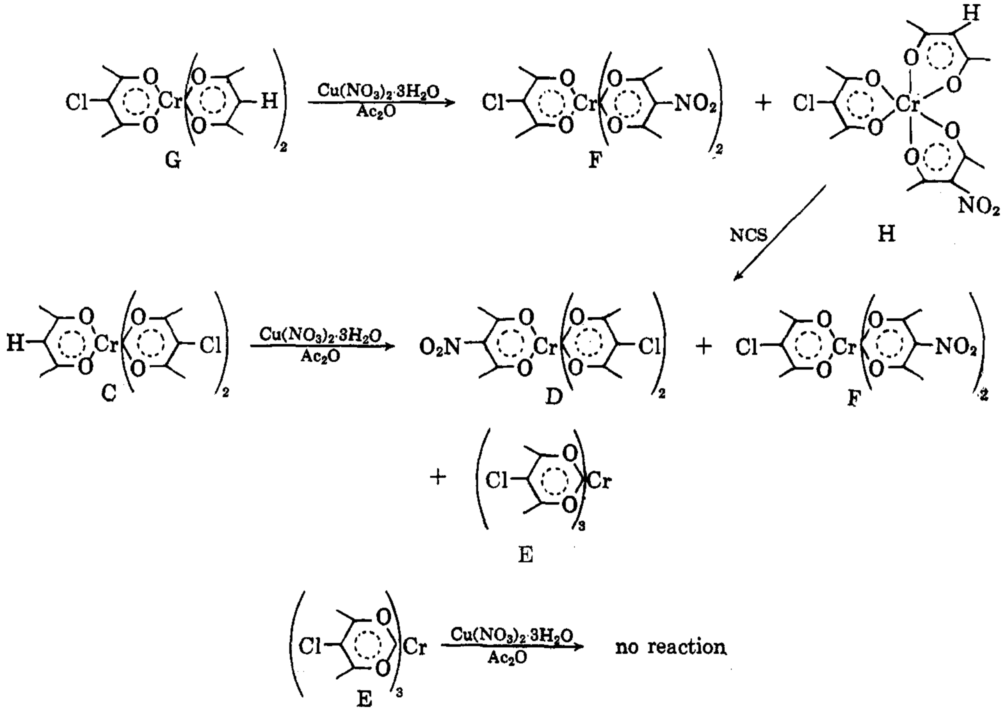
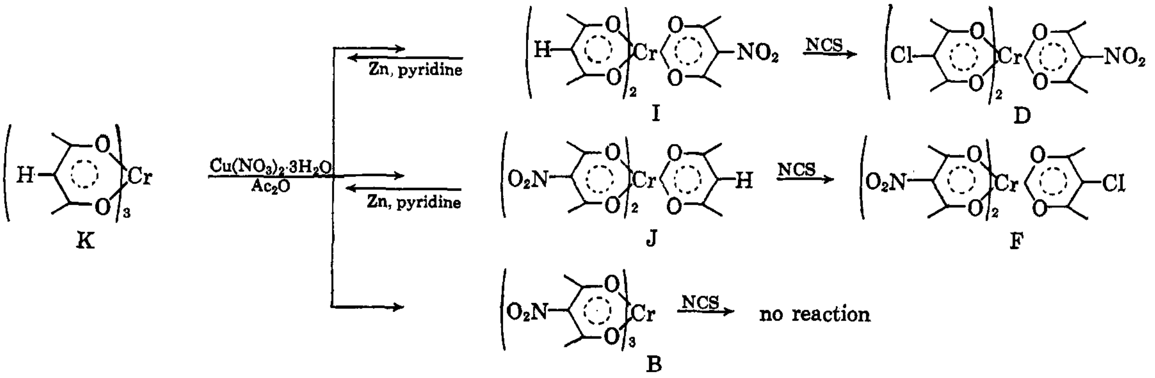


CHART II



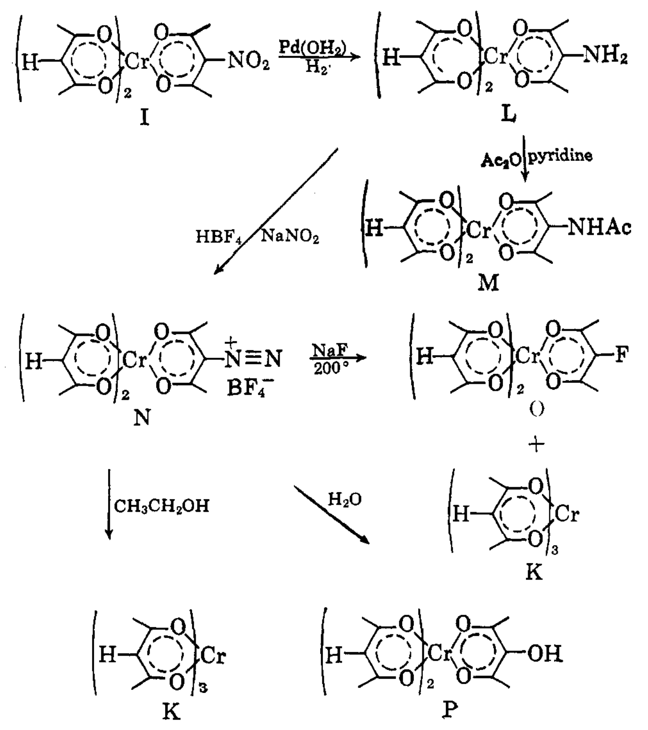
more fully this peculiar reaction, we carried out a nitration of the monochloro chromium chelate G under the same conditions. Two products, F and H, were separated and characterized from this reaction mixture, but neither of these compounds was derived from cleavage of chlorine atoms from the chelate ring. Treatment of the monchloro mononitro chromium chelate H with N-chlorosuccinimide (NCS) afforded the dichloro mononitro chelate identical with the product D isolated from nitrating the dichloro chromium chelate C (see Chart I), providing an extra check on the structures F, H, and D.

The structures of these mixed-ring chloro nitro chelates were further substantiated as the result of a series of experiments that were being conducted concurrently[5] with those described. Nitration of chromium acetylacetonate using limited amounts of the nitrating reagent afforded mixtures of the mononitro, dinitro, and trinitro chromium acetylacetonate. These partially nitrated chelates I, J, and B were easily separated by chromatography on Florisil. Chlorination of the dinitro chelate J afforded the dinitro monochloro chelate F in good yield. In the same way the mononitro dichloro chelate D was prepared from the mononitro chelate I. These reactions provided further support for the structures that were assigned to I, J, F, and D (see Chart II).

The ready accessibility of the mononitro chromium chelate I prompted us to use this substance as a precursor for the chelate amine and diazonium salt. Consequently, reductions of the chloronitro chelates were not attempted. Chemical reduction of the mononitro compound I with a wide variety of the usual reducing agents either failed to effect any transformation or gave rise to anomalous reactions. For example, treatment of the mononitro chelate I with zinc dust in pyridine at 60° afforded the unsubstituted acetylacetonate K. This surprising result involves reduction of the nitro group from an unsaturated carbon atom and replacement by hydrogen. A similar reaction was observed when the dinitro compound J was reduced with zinc dust in pyridine under the same conditions. However, under these conditions the trinitro chelate B afforded a very complex mixture which contained at least six components (as determined by thin layer chromatography experiments). This mixture did not contain the unsubstituted acetylacetonate K.

Catalytic hydrogenation of the nitro chelate I was more successful. Treatment of this nitro compound with hydrogen over palladium hydroxide afforded the

CHART III



monoamine L in good yield. The amino chelate L behaved as a normal aromatic amine forming stable salts with mineral acids, changing color upon salt formation, and reacting with acetic anhydride to afford an acetate derivative M. However, attempted hydrolysis of the N-acetyl group failed to yield the amine—probably because of the steric hindrance afforded by the flanking methyl groups on the chelate ring.

Treatment of an aqueous solution, the fluoroborate salt of the monamine L with a cold solution of sodium nitrite yielded a purple precipitate. This precipitate, which proved to be the pure chelate diazonium fluoroborate N was isolated by rapidly collecting the powder on a filter and washing repeatedly with anhydrous ether. The diazonium salt was decomposed by exposure to water or other nucleophilic solvents. However, aqueous solutions of the diazonium salt gave positive tests with β-naphthol. The structure of the chelate diazonium fluoroborate N is based on elemental analyses, a sharp infrared peak at 2200 cm.$^{-1}$ (diazonium ion), and reduction of the diazonium group to the unsubstituted chelate K by treatment with ethanol.

Attempted Sandmeyer reactions on the chelate diazonium salt were frustrated by the facile solvolysis of this ion. Hydrolysis of the chelate diazonium salt afforded a hydroxy-substituted chelate, which was isolated as a twelve hydrate. The water-soluble, hydroxy chelate behaved as a mild acid and was unstable in boiling solvents. All attempts to obtain this substance in its anhydrous form failed—although some of the waters of dehydration could be removed.

Initial attempts to effect a Schiemann reaction with the chelate diazonium salt by the usual procedures afforded tars and the unsubstituted acetylacetonate. However, sublimation of an intimate mixture of the powdered dry diazonium fluoroborate and anhydrous sodium fluoride at 200° under vacuum yielded a sublimate from which chromium acetylacetonate K and the monofluoro chromium chelate O could be separated by chromatography. The hitherto unknown fluoro-substituted chelate O was isolated in only 6% yield. The structure of this substance was assigned on the basis of elemental analyses and an infrared spectrum which exhibited carbon–fluorine stretching bands at 1490, 1320, and 1152 cm.$^{-1}$.

The chelate diazonium salt N exhibited good thermal stability, decomposing reproduceably from 165–167°. The salt was stored in a dry atmosphere for several months without any sign of decomposition.

Experiments in progress are designed to examine the mechanism of electrophilic cleavage of groups from unsymmetrically substituted chelate rings, and to carry out further transformations on the chelate diazonium salt.

Experimental

Nitration of Bis(2,4-pentanediono)(3-chloro-2,4-pentanediono)-chromium(III) (G).—A mixture of 1.0 g. (4.2 mmoles) of finely ground copper(II) nitrate trihydrate and 30 ml. of acetic anhydride was stirred for 45 min. at 0°. To this slurry was added 2.5 g. (6.5 mmoles) of monochlorochelate G, m.p. 197–198°. This reaction mixture was stirred for 4 hr. at 0°, allowed to come to room temperature, and then stirred for 1 more hr. This resulting mixture was poured into a mixture of 250 g. of ice, 150 ml. of water, and 20 g. of sodium acetate and stirred for 1 hr. The water layer was extracted three times with chloroform, and the combined chloroform extracts were washed with 5% aqueous sodium acetate solution and then water. After drying over sodium sulfate, the solvent was removed under vacuum. The resulting residue was purified by Florisil chromatography.

From the first band there was obtained 0.34 g. (10.7%) of bis(3-nitro-2,4-pentanediono)(3-chloro-2,4-pentanediono)-chromium(III) (F), m.p. 227°. The infrared spectrum was identical with that of a sample described later.

From the second band there was obtained 0.66 g. (23.6%) of (3-nitro-2,4-pentanediono)(3-chloro-2,4-pentanediono)-(2,4-pentanediono)chromium(III) (H), m.p. 205–208°. After recrystallization from ethanol, brown needles were obtained, m.p. 207–209°; infrared spectrum (KBr), 822 cm.$^{-1}$(NO_2) and 1200, 1270 cm.$^{-1}$ (unsubstituted C–H).

Anal. Calcd. for $C_{15}H_{19}O_8NClCr$: C, 42.01; H, 4.47; N, 3.27; Cl, 8.27. Found: C, 41.81; H, 4.38; N, 3.07; Cl, 8.12.

From the third band 0.52 g. (20.8%) of the starting material G was recovered.

Nitration of Bis(3-chloro-2,4-pentanediono)(2,4-pentanediono)chromium(III) (C).—A mixture of 0.95 g. (4.0 mmoles) of finely ground copper(II) nitrate trihydrate and 20 ml. of acetic anhydride was stirred for 45 min. at 0°. To this slurry was added 1.5 g. (3.6 mmoles) of dichloro chelate C, m.p. 199–200°. This reaction mixture was stirred for 4 hr. at 0°, allowed to come to room temperature, and then stirred for 1 more hr. The resulting slurry was poured into a mixture of 150 g. of ice, 70 ml. of water, and 12 g. of sodium acetate, and then stirred for 1 hr. to decompose the acetic anhydride. The water layer was extracted three times with chloroform and the combined chloroform extracts were washed with 5% aqueous sodium acetate solution and then with water. After drying over sodium sulfate, the solvent was evaporated under diminished pressure. The residue was purified by Florisil chromatography.

From the first band there was obtained 0.17 g. (19.5%) of tris(3-chloro-2,4-pentanediono)chromium(III) (E), yellow needles, m.p. 207–208°. The infrared spectrum was identical with that of an authentic sample.[8]

The second fraction eluted with benzene afforded 0.20 g. (12.0%) of bis(3-chloro-2,4-pentanediono)(3-nitro-2,4-pentanediono)chromium(III) (D). After recrystallization from ethanol, yellow-brown hexagonal plates were obtained, m.p. 204–204.5°; infrared spectrum (KBr), 823, 1520 cm.$^{-1}$ (–NO_2).

Anal. Calcd. for $C_{15}H_{18}O_8NCl_2Cr$: C, 38.89; H, 3.93. Found: C, 39.03; H, 4.09.

From the third band 0.18 g. (10.6%) of bis(3-nitro-2,4-pentanediono)(3-chloro-2,4-pentanediono)chromium(III) (F), m.p. 227° was obtained. The infrared spectrum was identical with that of an authentic sample.

From the fourth band 0.19 g. (12.7%) of the starting material C was recovered.

Nitration of Tris(3-chloro-2,4-pentanediono)chromium(III) (E).—A mixture of 0.88 g. (3.63 mmoles) of finely ground copper(II) nitrate trihydrate and 20 ml. of acetic anhydride was stirred for 45 min. at 0°. To this slurry was added 1.5 g. (3.3 mmoles) of chloro chelate E,[8] m.p. 207–208°. This reaction mixture was stirred for 4 hr. at 0°, allowed to come to room temperature, and then stirred for 1 more hr. The resulting mixture was poured into a slurry of 150 g. of ice, 70 ml. of water, and 12 g. of sodium acetate, and stirred for 1 hr. to decompose the acetic anhydride. The water layer was extracted three times with chloroform and the combined chloroform extracts were washed with 5% aqueous sodium acetate solution and then with water. After drying over sodium sulfate, the solvent was removed under vacuum. The resulting residue was purified by Florisil chromatography, and 1.02 g. of the starting material E, m.p. 209°, was recovered. The infrared spectrum was identical with that of an authentic sample.[8] The yield of recovered starting material was 68.0%.

Chlorination of (3-Nitro-2,4-pentanediono)(3-chloro-2,4-pentanediono)(2,4-pentanediono)chromium(III) (H).—To a boiling solution of the 100 mg. of nitrochloro chelate H in 5 ml. of chloroform was added 100 mg. of N-chlorosuccinimide in 2 ml. of chloroform with vigorous stirring. The reaction mixture was heated at reflux for 1 hr., cooled to room temperature, and washed with 5% aqueous sodium sulfite solution and then with water. After drying the organic layer over sodium sulfate, the solvent was removed under vacuum. The residue was recrystallized from ethanol, and 63 mg. (58.3%) of bis(3-chloro-2,4-pentanediono)(3-nitro-2,4-pentanediono)chromium(III) (D), m.p. 204.5°, was obtained.

Nitration of Tris(2,4-pentanediono)chromium(III) (K).—A mixture of 3.1 g. (12.9 mmoles) of finely ground copper(II) nitrate trihydrate and 200 ml. of acetic anhydride was stirred for 30 min. at 0°. To this slurry was added 7.5 g. (21.5 mmoles) of chelate K. The reaction mixture was stirred for 3 hr. at 0°, allowed to come to room temperature, and then stirred for 1 more hr. The resulting solution was poured into a slurry of 900 g. of ice, 900 ml. of water, and 22 g. of sodium acetate, and stirred for 1 hr. The water layer was extracted three times with chloroform and the combined chloroform extracts were washed four times with 5% aqueous sodium acetate solution and once with water. The organic layer was dried over sodium sulfate, and then removed under reduced pressure. The resulting residue was separated and purified by chromatography on Florisil (deactivated with 10% water) with benzene as the eluent.

From the first band 0.71 g. of bis(3-nitro-2,4-pentanediono)-(2,4-pentanediono)chromium(III) (J), 7.5% yield, was obtained. After recrystallization from chloroform–ethanol, brown needles were obtained, m.p. 246–246.5°.

Anal. Calcd. for $C_{15}H_{19}O_{10}N_2Cr$: C, 41.01; H, 4.36; N, 6.38. Found: C, 41.30; H, 4.37; N, 6.44.

From the second band 5.46 g. of bis(2,4-pentanediono)(3-nitro-2,4-pentanediono)chromium(III) (I), 64.5% yield, was obtained. After recrystallization from ethanol, brown prisms were obtained, m.p. 178–180°.

Anal. Calcd. for $C_{15}H_{20}O_8NCr$: C, 45.69; H, 5.11; N, 3.55. Found: C, 46.14; H, 5.32; N, 3.89.

From the acetone eluent 0.88 g. (11.7%) of starting material K was recovered.

Chlorination of Bis(2,4-pentanediono)(3-nitro-2,4-pentanediono)chromium(III) (I).—To a boiling solution of 100 mg. of nitro chelate I in 5 ml. of chloroform was added a solution of 200 mg. of N-chlorosuccinimide in 3 ml. of chloroform. The slurry was heated at reflux for 1 hr. and then cooled to room temperature. The reaction mixture was washed with 5% aqueous sodium sulfite solution and then with water. After drying over sodium sulfate, the solvent was evaporated under vacuum. The resulting residue was purified by chromatography on deactivated Florisil (10% water).

From the benzene eluent 80 mg. (68.0%) of bis(3-chloro-2,4-pentanediono)(3-nitro-2,4-pentanediono)chromium(III) (D), m.p. 204–204.5°, was obtained. The infrared spectrum was identical with that of an authentic sample of D.

Chlorination of Bis(3-nitro-2,4-pentanediono)(2,4-pentanediono)chromium(III) (J).—To a boiling solution of 300 mg. of nitro chelate J in 15 ml. of chloroform was added 300 mg. of N-chlorosuccinimide in 15 ml. of chloroform. The slurry was heated under reflux for 1 hr. and then cooled to room temperature. The reaction mixture was washed with 5% aqueous sodium sulfite solution and then with water. After drying over sodium sulfate, the solvent was removed under vacuum. The resulting residue was separated and purified by chromatography on Florisil (deactivated with 10% water).

From the first benzene eluent 100 mg. of bis(3-nitro-2,4-pentanediono)(3-chloro-2,4-pentanediono)chromium(III) (F), m.p. 225–226° (30.9% yield), was obtained. The infrared spectrum was identical with that of an authentic sample.

From the second benzene eluent 140 mg. of starting material J (46.7% yield) was recovered.

Treatment of Bis(2,4-pentanediono)(3-nitro-2,4-pentanediono)chromium(III) (I) with Zinc Dust.—To a mixture of 1.5 g. of nitro chelate I, 1.5 g. of zinc dust, and 20 ml. of pyridine was added 3 ml. of glacial acetic acid, keeping the temperature at 60°. The mixture was stirred for 3 hr. at 60–70°. After cooling to room temperature, the reaction mixture was poured into a mixture of 150 g. of ice and 150 ml. of water. The water layer was extracted with chloroform. The organic layer was removed, dried over sodium sulfate, and then evaporated under reduced pressure. The resulting residue was purified by use of Florisil (deactivated with 10% water). From the benzene eluent 0.35 g. of tris(2,4-pentanediono)chromium(III) (K), m.p. 210–211° (25.7% yield), was obtained. The infrared spectrum was identical with that of an authentic sample.

Treatment of Bis(3-nitro-2,4-pentanediono)(2,4-pentanediono)chromium(III) (J) with Zinc Dust.—To a mixture of 0.8 g. of the nitro chelate J, 1.5 g. of zinc dust, and 10 ml. of pyridine was added 3 ml. of glacial acetic acid, keeping the temperature at 60°. The slurry was stirred for 3 hr. at 60–70°. The reaction mixture was cooled to room temperature and poured into 150 ml. of ice water. The water layer was extracted with chloroform. The organic layer was removed, dried over sodium sulfate, and then the solvent was evaporated under vacuum. The resulting residue was purified by chromatography on Florisil (deactivated with 10% water). From the benzene eluent was obtained 70 mg. of tris(2,4-pentanediono)chromium(III) (K), m.p. 210–211° (11.0% yield). The infrared spectrum was identical with that of an authentic sample.

Bis(2,4-pentanediono)(3-amino-2,4-pentanediono)chromium(III) (L).—A mixture of 6.0 g. of nitro chelate I, 2.0 g. of palladium hydroxide and 250 ml. of absolute ethanol (the chelate I was not completely dissolved in ethanol) was shaken in a Paar hydrogenator under 65 lb. pressure at room temperature for 24 hr. The catalyst was removed by filtration and washed with ethanol until the filtrate was colorless. The combined solvent was evaporated under vacuum. The residue was purified by chromatography on Florisil using benzene containing 5% methanol as the eluent. From the third band 3.83 g. of bis(2,4-pentanediono)(3-amino-2,4-pentanediono)chromium(III) (L) was obtained, m.p. 221–223° (69.1% yield). After recrystallization from benzene, brownish crystals were obtained, m.p. 221.5–223°.

Anal. Calcd. for $C_{15}H_{22}O_6NCr$: C, 49.44; H, 6.09; N, 3.85; mol. wt., 364.35. Found: C, 49.29; H, 6.13; N, 3.67; mol. wt., 412.

Acetylation of Bis(2,4-pentanediono)(3-amino-2,4-pentanediono)chromium(III) (L).—To a mixture of 100 mg. of amino chelate L and 2 ml. of acetic anhydride was added several drops of pyridine. This slurry was stirred at room temperature for 24 hr. and then poured into 100 g. of ice water containing 2 g. of sodium acetate. The water layer was extracted three times with chloroform. The combined solvent was washed with water and then dried over sodium sulfate. After the solvent was removed, a purple solid remained, m.p. 255–258°. The yield of acetylamino chelate M was 90 mg. (80.7%). After recrystallization from ethanol–petroleum ether, purple needles were obtained, m.p. 259.5–261°.

Anal. Calcd. for $C_{17}H_{24}O_7NCr$: C, 50.24; H, 5.95; N, 3.45. Found: C, 49.54; H, 5.92; N, 3.42.

Diazotization of Bis(2,4-pentanediono)(3-amino-2,4-pentanediono)chromium(III) (L).—Amino chelate L (0.73 g., 2.0 mmoles) was dissolved in a cold (0°) solution of 1.08 g. of 48% fluoroboric acid (6.0 mmoles) and 4.0 g. of water. To this solution was added 1.52 g. of a 10% aqueous sodium nitrite solution (2.2 mmoles of sodium nitrite) at 0° for 5 min. with vigorous stirring. A pale purple precipitate appeared. After stirring for 5 min., the purple solid was quickly collected by filtration and washed with cold absolute ethanol and then with cold ether. If this collection and washing steps were not accomplished quickly, the precipitate became sticky and decomposed. The yield of chelate diazonium fluoroborate N was 0.51 g. (55.0%). The infrared spectrum exhibited a sharp peak at 2200 cm.$^{-1}$ (diazonium ion[18]) and a peak at 1050 cm.$^{-1}$ (fluoroborate anion[19]). The diazonium salt melted at 165° with decomposition.

Anal. Calcd. for $C_{15}H_{20}O_6N_2CrBF_4$: C, 38.90; H, 4.35; N, 6.05. Found: C, 38.67; H, 4.32; N, 6.17.

Reduction of the Chelate Diazonium Fluoroborate N with Ethanol.—A solution of 50 mg. of the chelate diazonium fluoroborate N in 2 ml. of absolute ethanol was heated at reflux on the steam bath for 2 hr. After the solvent was removed under vacuum, the resulting residue was purified by chromatography on Florisil using benzene. From the benzene eluent 15 mg. of tris(2,4-pentanediono)chromium(III) (K), m.p. 201–204° (40% yield), was obtained. After recrystallization from benzene–petroleum ether, the sample melted at 210–211°. The infrared spectrum was identical with that of an authentic sample.

Pyrolysis of the Chelate Diazonium Fluoroborate N.—A mixture of 1.0 g. of the chelate diazonium fluoroborate N and 4.0 g. of powdered sodium fluoride was heated at 180–200° (oil bath temperature) for 8 hr. under vacuum (0.5 mm.) in a sublimation apparatus. The sublimate weighed 240 mg. This solid was separated by chromatography on Florisil (deactivated with 10% water) using benzene. From the second benzene eluent was obtained 50 mg. of bis(2,4-pentanediono)(3-fluoro-2,4-pentanediono)chromium(III) (O), m.p. 208–210° (6.3% yield). After recrystallization from petroleum–ether, the melting point was 212.5–213.5°. The infrared spectrum exhibited selected maxima at 1490, 1320, and 1152 cm.$^{-1}$.

Anal. Calcd. for $C_{15}H_{20}O_6FCr$: C, 49.04; H, 5.49; F, 5.17. Found: C, 48.76; H, 5.31; F, 4.72.

From the third benzene eluent 120 mg. of tris(2,4-pentanediono)chromium(III) (K), m.p. 209–211° (15.9% yield), was obtained. The infrared spectrum of this substance was identical with that of tris(2,4-pentanediono)chromium(III) (K).

Decomposition of the Chelate Diazonium Fluoroborate N in Water.—The chelate diazonium fluoroborate N (200 mg.) was dissolved in 2 ml. of water. This solution was warmed at 35–40° for 2 hr. and then extracted with a large amount of ether. The ether layer was separated and the solvent was removed under vacuum (at room temperature). The resulting residue weighed 130 mg., m.p. 121–123°. After recrystallization from ethanol-benzene, purple cubic crystals were obtained, m.p. 121–123.

Anal. Calcd. for $C_{15}H_{21}O_7Cr\cdot 12H_2O$: C, 30.97; H, 7.80. Found: C, 30.71; H, 7.60.

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Direct Synthesis of Ternary Iminium Salts by Combination of Aldehydes or Ketones with Secondary Amine Salts[1,2]

NELSON J. LEONARD AND JOSEPH V. PAUKSTELIS

Noyes Chemical Labaratory, University of Illinois, Urbana, Illinois

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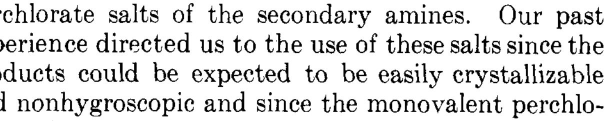
A general reaction for the preparation of ternary iminium perchlorates, $>C{=}\overset{+}{N}<\ ClO_4^-$, is found in the simple combination of an aldehyde or a ketone with a secondary amine perchlorate (Table I). The yields are excellent in the absence of serious steric interference. In the n.m.r. spectra of representative iminium salts, long-range coupling has been observed through three single bonds and the iminium bond and through four single bonds and the iminium bond. Mesityl oxide is converted to N-isopropylidenepyrrolidinium perchlorate (VI) by reaction with pyrrolidine perchlorate, thereby providing an efficient dealdolization process.

The importance of the $>C{=}\overset{+}{N}<\ X^-$ function in organic chemistry has been well documented by Hellmann and Opitz.[3] Immonium salts[4] or ternary iminium salts[5] (we prefer the latter name) occupy a key position in many organic reactions and are subject to rapid attack by a wide variety of nucleophilic reagents.[3,6] The salts are generally made by cleavage of a covalent C–Y bond in a $>N{-}\overset{|}{\underset{|}{C}}{-}Y$ system,[4,7] by alkylation of aldimines or ketimines,[4] and by protonation of enamines.[4,8] It is also possible to obtain ternary iminium complex salts by direct combination of an aldehyde or ketone with a secondary amine complex salt, *e.g.*; hexahalostannates,[5,9-11] halobismuthates,[5,9-10] haloantimonates,[5,9-11] hexahaloplatinates,[9,10] or iodide–silver iodide complexes.[12]

We have now found an adaptation of this procedure, which is simple and generally useful, employing the perchlorate salts of the secondary amines. Our past experience directed us to the use of these salts since the products could be expected to be easily crystallizable and nonhygroscopic and since the monovalent perchlorate anion, being a poor nucleophile, would not interfere with reaction products sought beyond the ternary iminium stage.[8b] The general reaction which can be effected is that of a ketone or aldehyde with a secondary amine perchlorate to give a ternary iminium perchlorate.



(1)

As an example of the ease with which conversion occurs, the mixing of pyrrolidine perchlorate with a slight excess of acetone liberates heat and produces crystalline N-isopropylidenepyrrolidinium perchlorate

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(2) Presented at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963.

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