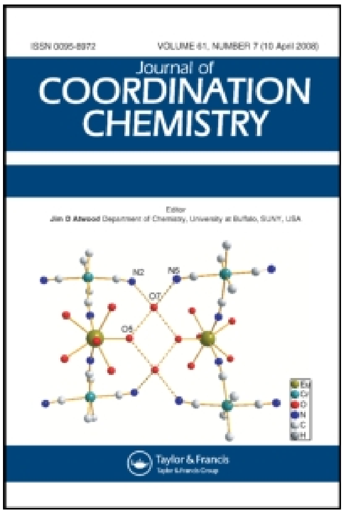

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NOTE

DIAZO COUPLING OF METAL CHELATES OF 2,4-PENTANEDIONE

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Metal 1,3-diketonates are known to undergo many electrophilic substitutions typical of aromatic compounds because of the *quasi*-aromatic C_3O_2M ring systems present in these chelates.[1] Although the aryldiazonium ion is a dominant electrophile (its coupling with free 1,3-diketones is an electrophilic substitution), reports are scanty on its reaction with metal-chelated 1,3-diketones. In this paper, we report the electrophilic substitution of the phenyldiazonium ion at 2,4-pentanedionates of aluminum(III), chromium(III), copper(II) and palladium(II).

EXPERIMENTAL

Aluminum(III), chromium(III), copper(II) and palladium(II) chelates of 2,4-pentanedione (acetylacetone) were prepared by the procedures published in the literature.[2] Phenyldiazonium chloride was obtained through the diazotization of aniline using sodium nitrite and hydrochloric acid. Excess nitrous acid present in the diazonium salt solution was destroyed by adding urea. The coupling reaction was carried out as follows.

To a solution of metal 1,3-diketonates (0.001 mol) in methanol (5 cm^3), kept below 5°C in an ice-salt bath, was added slowly with stirring a cold aqueous solution of the diazonium salt (0.003 mol in the case of the tris chelates of Al(III) and Cr(III), and 0.002 mol in the case of the bis chelates of Cu(II) and Pd(II)). A solution of sodium hydroxide (10^{-3} M) was used to maintain the pH of the mixture between 9 and 10. The precipitated product was filtered, washed with water, sucked dry, recrystallized from hot ethanol and dried in vacuum. Physical and analytical data for the products are given in Table I.

Infrared spectra of the compounds were recorded on a Shimadzu IR 435 spectrometer in KBr pellets, and NMR spectra on a Varian XL-100 FT NMR spectrometer in $CDCl_3$ solution.

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TABLE I
Physical and analytical data for the diazo coupled products.

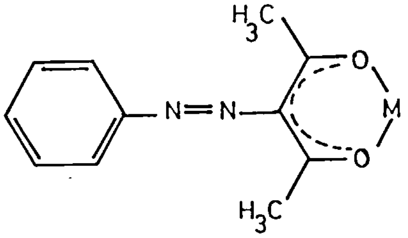
Diazo coupled product of[a]	M.P. (°C)	Colour	Found % M	Found % C	Found % H	Found % N	Calculated[b] % M	Calculated[b] % C	Calculated[b] % H	Calculated[b] % N
$Cr(acac)_3$	170	Red	6.9	58.5	4.4	12.0	7.9	59.9	5.0	12.7
$Pd(acac)_2$	180	Brown		50.5	4.0	9.0		51.5	4.3	10.9
$Al(acac)_3$	110	Red	3.9	61.3	4.9	13.0	4.3	62.3	5.2	13.2
$Cu(acac)_2$	198	Black	13.3	55.6	4.5	12.4	13.5	56.2	4.7	13.2

[a] Acac = acetylacetonate ion. [b] Calculated values are based on the structure given.

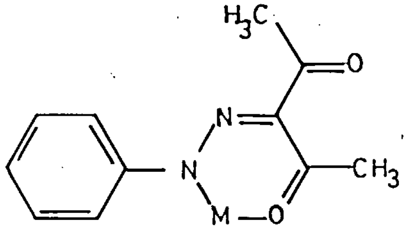
RESULTS AND DISCUSSION

That substitution of phenylazo group has occurred on the chelate rings of the metal acetylacetonates was tested by reductive cleavage of the azo function using zinc and acetic acid.[3] The aniline formed during the reduction was extracted with ether, diazotized in the usual way and coupled with alkaline 2-naphthalenol. The resulting orange-red product was identified as 1-(phenylazo)-2-naphthalenol on comparison with an authentic sample. Elemental analyses of the diazo coupled products indicate that substitution has occurred on all the chelate rings of the metal acetylacetonates.

Infrared spectra of the diazo coupled products of chromium(III) and palladium(II) chelates of acetylacetone are in accord with structure **1**, while those of aluminum(III) and copper(II) with structure **2**.



(1)



(2)

Thus, the i.r. spectra of the former compounds are characterized by the absence of any absorption in the region 1600–1750 cm^{-1} (indicating that both the carbonyl groups are engaged in bonding with metal ion), the presence of an intense band at about 1580 cm^{-1} for the metal bonded carbonyl group, and two strong bands at about 1520 cm^{-1} (C=C stretching) and 1380 cm^{-1} (C=O asymmetric stretching) as in metal acetylacetonates.[4] A weak band at 1435 ± 5 cm^{-1} in the spectra is assignable to N=N stretching.[5] The spectrum of the chromium(III) complex shows two medium intensity bands at 460 and 335 cm^{-1} due to Cr–O stretching;[4] the corresponding bands of the palladium(II) complex appear at 442 and 295 cm^{-1}.

The i.r. spectra of the diazo coupled products of aluminum(III) and copper(II) show a strong band at about 1670 cm^{-1} due to free acetyl carbonyl and a strong band at about 1555 cm^{-1} for the metal chelated carbonyl. The absence of the 1435 cm^{-1} band due to N=N and the occurrence of a medium intensity band at about 1612 cm^{-1} assignable to the stretching of C=N of the hydrazone function are in agreement with structure **2**.[6] Two medium intensity bands at about 550 and 445 cm^{-1} due to M–N and M–O, respectively, are also observed in the spectra of these compounds. The spectrum of the copper(II) chelate closely resembles that of the copper(II) chelate of 3-phenylhydrazeno-2,4-pentanedione, reported earlier.[7] Spectra of all compounds show characteristic absorptions for aliphatic C–H at about 2870 and 2970 cm^{-1} and for aromatic C–H at about 3050 cm^{-1}.

The proton n.m.r. spectra of the diamagnetic aluminum(III) and palladium(II) chelates also support their formulations. Thus, the methylenic proton signal characteristic of metal acetylacetonates is absent in the spectra of the diazo coupled products, a fact which indicates that substitution has occurred on all chelate rings. The spectra of the aluminum(III) chelate shows two methyl resonance peaks of equal intensity at 2.28δ and 2.42δ. Such splitting is possible with structure **2**, which has the two methyl groups non-equivalent.[8] The spectrum of the palladium(II) chelate shows only a single methyl resonance signal at 2.20δ, indicating that its methyl protons are in identical environments, in agreement with structure **1**. The integrated intensities of the phenyl proton signals (about 7.5δ) and methyl proton signals agree well with the proposed structures.

It has been shown that arylazo derivatives of 1,3-diketones exist entirely as intramolecularly hydrogen bonded 2-arylhydrazones. This form persists in metal complexes, in which the hydrogen bonded carbonyl and one of the hydrazeno nitrogens bond with the metal, leaving one of the carbonyl groups free. In the case of phenylazo substitution of metal acetylacetonates, no rearrangement occurs if the metal chelate is very stable (*e.g.* structure **1** for the chromium(III) and palladium(II) chelates). Otherwise, rearrangement of the ligand to the 2-phenylhydrazeno-2,4-pentanedionate (*e.g.* structure **2** for the aluminum(III) and copper(II) chelates) occurs readily.

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