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REACTIONS OF ORGANIC NITROSO COMPOUNDS WITH DISODIUM DECACARBONYLDICHROMATE

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Summary

The sodium salt $Na_2Cr_2(CO)_{10}$ reacts with nitrosobenzene to give azobenzene in excellent yield. However, a similar reaction of $Na_2Cr_2(CO)_{10}$ with 2-methyl-2-nitrosopropane dimer gives the t-butylamine complex $(CH_3)_3CNH_2Cr(CO)_5$.

Introduction

The reaction of $Na_2Cr_2(CO)_{10}$ with 2-bromo-2-nitrosopropane was recently reported [1, 2] to give the dimethylketimine complex $(CH_3)_2C{=}N(H)Cr(CO)_5$. In an attempt to provide some insight into this apparently curious reaction, some reactions of simpler organic nitroso compounds with $Na_2Cr_2(CO)_{10}$ have now been examined.

Experimental

Commercial hexacarbonylchromium (Pressure Chemical Corp., Pittsburgh, Pa.), after resublimation, was converted to the sodium salt $Na_2Cr_2(CO)_{10}$ by ultraviolet irradiation in tetrahydrofuran solution for 24 h in the presence of excess 0.75% sodium amalgam with vigorous stirring. t-Butylamine and nitrosobenzene were commercial products whereas 2-methyl-2-nitrosopropane was prepared by a published procedure [3]. Other general aspects of the experimental procedure are similar to those given in previous papers from this laboratory [2].

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Reaction of $Na_2Cr_2(CO)_{10}$ with nitrosobenzene

A solution of $Na_2Cr_2(CO)_{10}$ prepared from 11 g (50 mmol) of $Cr(CO)_6$ in 150 ml of tetrahydrofuran was stirred with 2.7 g (25.3 mmol as monomer) of nitrosobenzene for 8 h. The reaction mixture was then filtered on Celite and the Celite washed with 200 ml of dichloromethane. Removal of solvent (~ 25°/ 25 mm) from the combined tetrahydrofuran filtrate and dichloromethane washings followed by chromatography of the residue on Florisil gave a large orange band. Elution of this band with hexane followed by evaporation of the eluate gave 1.97 g (92% yield based on nitrosobenzene) of azobenzene identified by its m.p. and proton NMR spectrum.

Reaction of $Na_2Cr_2(CO)_{10}$ with azoxybenzene

A solution of $Na_2Cr_2(CO)_{10}$ prepared from 6.6 g (30 mmol) of $Cr(CO)_6$ in 150 ml of tetrahydrofuran was stirred with 2.0 g (10 mmol) of azoxybenzene at room temperature for 3 h. The resulting orange-brown reaction mixture was then filtered. Solvent and excess $Cr(CO)_6$ were removed in vacuum. Chromatography of the residue on Florisil in hexane solution gave 1.43 g (77% yield based on azoxybenzene) of azobenzene.

Reaction of $Na_2Cr_2(CO)_{10}$ with 2-methyl-2-nitrosopropane

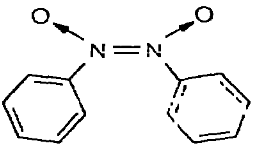
A solution of $Na_2Cr_2(CO)_{10}$ prepared from 11 g (50 mmol) of $Cr(CO)_6$ in 250 ml of tetrahydrofuran was stirred for 20 h with 7.5 g (86 mmol as monomer) of dimeric 2-methyl-2-nitrosopropane. The reaction mixture was then filtered and solvent removed from the filtrate at ~ 25°/35 mm. Chromatography of the residue on alumina in hexane solution gave a bright yellow band, which after elution with hexane and recrystallization from hexane gave 1.3 g (10 % yield) of yellow flakes of $(CH_3)_3CNH_2Cr(CO)_5$ m.p. 94-96°; infrared ν(CO): 2074 w, 1934 w, and 1919 s cm^{-1}; proton NMR ($CDCl_3$): τ 8.30 (broad singlet: NH_2) and τ 8.90 (sharp singlet: CH_3). Anal. Found: C, 40.9; H, 4.4; N, 5.1. $C_9H_{11}CrNO_5$ calcd.: C, 40.8; H, 4.2; N, 5.3%.

This product was identical to authentic $(CH_3)_3CNH_2Cr(CO)_5$ made by the following adaptation of a published procedure [4]. A mixture of 10 g (45 mmol) of $Cr(CO)_6$, 3.0 g (40 mmol) of t-butylamine, and 250 ml of tetrahydrofuran was exposed to UV irradiation for 8 h. Filtration, removal of solvent from the filtrate at ~ 25°/25 mm, and chromatography of the residue on a 2 × 100 cm Florisil column gave 3.6 g (33% yield) of yellow $(CH_3)_3CNH_2Cr(CO)_5$, m.p. 95-97°, identical to the product obtained from $Na_2Cr_2(CO)_{10}$ and 2-methyl-2-nitrosopropane as described above.

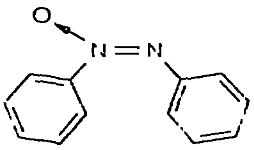
Discussion

Differences in the state of aggregation of the reactive forms of nitrosobenzene and 2-methyl-2-nitrosopropane can account for the observed differences in their reactions with $Cr_2(CO)_{10}^{2-}$. Thus, deoxygenation of nitrosobenzene dimer (I) with $Cr_2(CO)_{10}^{2-}$ provides an obvious route to azobenzene. The ability of $Cr_2(CO)_{10}^{2-}$ to deoxygenate structures of this type is demonstrated by its reaction with azoxybenzene (II) to give a good yield of azobenzene. Similar deoxygenation of monomeric 2-methyl-2-nitrosopropane with $Cr_2(CO)_{10}^{2-}$ would give the nitrene $(CH_3)_3CN$, which apparently complexes with a $Cr(CO)_5$ unit and undergoes further reduction to the observed $(CH_3)_3CNH_2Cr(CO)_5$.

The structural similarity between 2-methyl-2-nitrosopropane and 2-bromo-2-nitrosopropane suggests that the initial product of the reaction of the latter with $Cr_2(CO)_{10}^{2-}$ is the halogenated amine complex $(CH_3)_2C(Br)NH_2Cr(CO)_5$. Elimination of hydrogen bromide from this complex provides a facile route to $(CH_3)_2C{=}NHCr(CO)_5$, which is the observed stable product [1,2] from 2-bromo-2-nitrosopropane and $Na_2Cr_2(CO)_{10}$.



(I)



(II)

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References

1 R.B. King and W.M. Douglas, J. Amer. Chem. Soc., 95 (1973) 7528.
2 R.B. King and W.M. Douglas, Inorg. Chem., 13 (1974) 1339.
3 W.D. Emmons, J. Amer. Chem. Soc., 79 (1957) 5739, 6522.
4 R.J. Dennenberg and D.J. Darensbourg, Inorg. Chem., 11 (1972) 72.