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Preliminary communication

THE DIPHENYLMETHYLBIS(π-CHROMIUM TRICARBONYL) CARBONIUM ION.ISOLATION OF A STABLE HEXAFLUOROPHOSPHATE SALT

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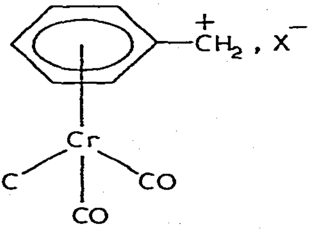
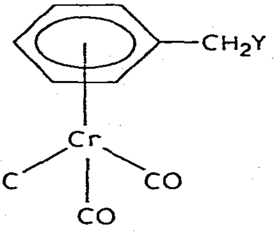
Summary

Reaction of diphenylmercurybis(π-chromium tricarbonyl) with dicobalt octacarbonyl in THF gave benzophenonebis(π-chromium tricarbonyl). Reduction of the latter with $NaBH_4$ in methanol resulted in formation of the expected alcohol which was treated with hexafluorophosphoric acid in propionic anhydride to give the title carbonium ion salt as a blue solid. This salt was found to alkylate ethanol, diethylamine and pyrrole.

The ability of a benzenechromium tricarbonyl unit to assist in the stabilization of an adjacent carbonium ion center has been the subject of some interest. Pettit and coworkers [1] attempted, unsuccessfully, to prepare a stable π-complexed carbonium ion salt of type I. Treatment of IIa with $HClO_4$ and HBF_4 in acetic anhydride resulted in a rapid reaction, but no stable I could be isolated. Rapid decomposition occurred while carbon monoxide was evolved. Treatment of IIb with $AgClO_4$, $AgBF_4$ or $SbCl_5$ in nitromethane resulted in similar decomposition. Even attempts to prepare stable,

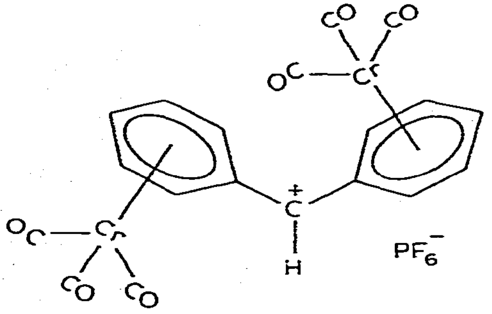


(I)



(IIa) Y = OH
(IIb) Y = Cl

charged, $Cr(CO)_3$-complexed species in which the free ligand itself was known to form stable carbonium ions, under similar reaction conditions, resulted in decomposition with loss of CO. It was suggested that such decarbonylation occurred because electron density was transferred to the cationic ligand in these complexes at the expense of the stabilizing back-donation to the CO ligands and that these observations thus had no real bearing on the question of the stabilization of carbocations such as I by chromium. The observed rate enhancement of the solvolysis of IIb by a factor of 10^5 vs. uncomplexed benzyl chloride [1] and the experimental determination of $pK_R = -11.8$ for I in concentrated sulfuric acid solution [2] (vs. a value of < -17.3 for $PhCH_2^+$) provided evidence that I was indeed stabilized by the presence of the π-complexed $Cr(CO)_3$ substituent.

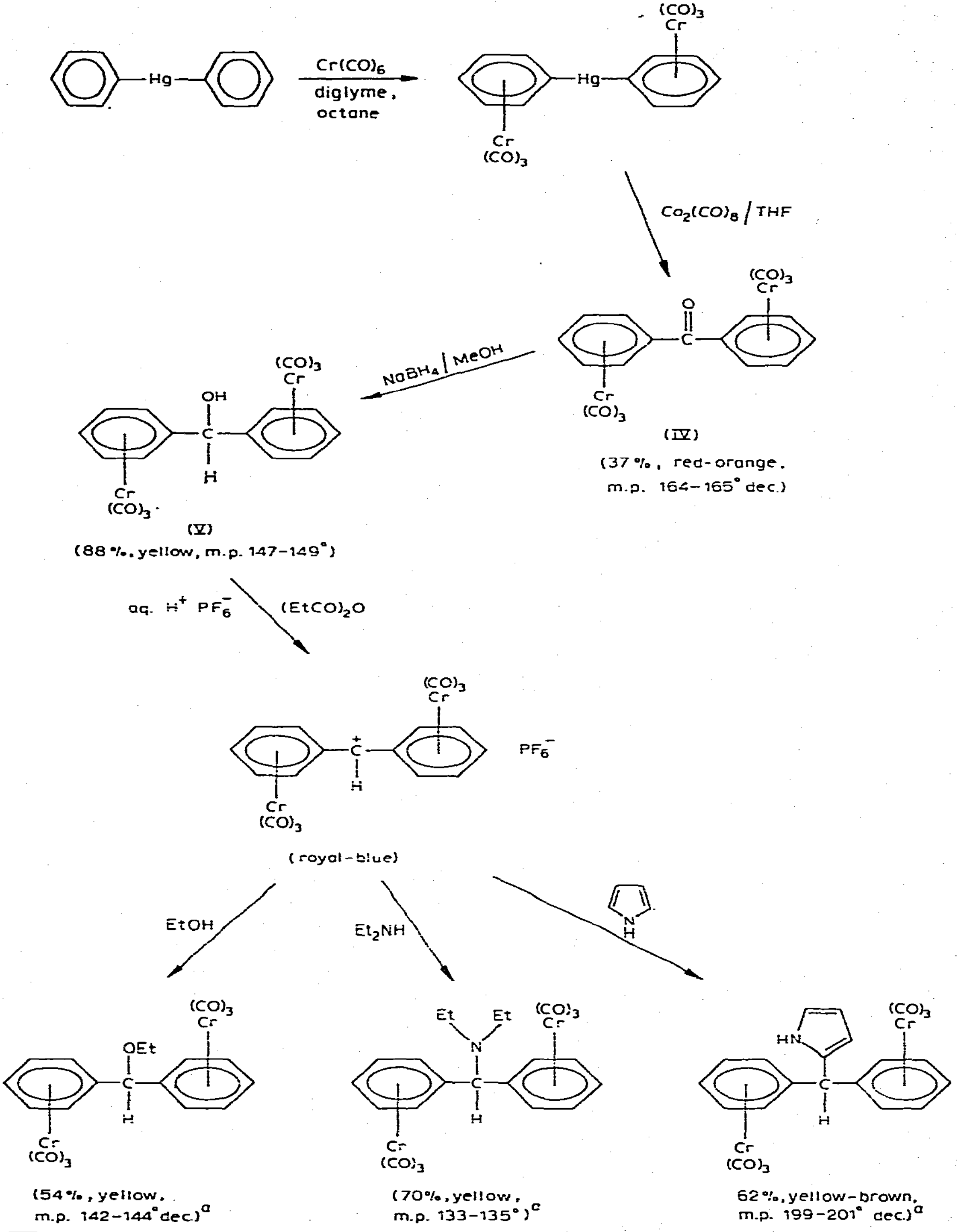


(III)

We have been able to prepare an isolable carbonium ion salt containing two π-benzenechromium tricarbonyl units, III. The preparative sequence to III, which is shown in Scheme 1, is based on the known diphenylmercurybis-(π-chromium tricarbonyl) [3,4] and its reaction with dicobalt octacarbonyl at room temperature [5] to give the red-orange ketone IV. A slurry of the latter in methanol was reduced with sodium borohydride to give the yellow carbinol V. Treatment of V in the form of a slurry in degassed propionic anhydride with a solution of 65% aqueous HPF_6 in propionic anhydride under nitrogen imparted a blue-green color to the mixture and caused separation of a royal blue solid. The chemistry of this solid is consistent with its formulation as III (Scheme 1). This carbonium ion salt appears to be considerably more reactive than the diferrocenylmethyl carbonium ion, whose perchlorate salt is reported to decompose slowly in alcohols [6] and whose tetrafluoroborate salt could be recrystallized and recovered unchanged from methanol [7]. The "*transoid*" arrangement of the $Cr(CO)_3$ groups in III is suggested in view of the known structures of biphenylbis(π-chromium tricarbonyl) [8] and diferrocenylmethyl tetrafluoroborate [7], both of which have such a disposition of metal atoms.

The ^{13}C NMR spectrum of alcohol V in acetone-d_6 showed the C-OH carbon resonance at δ 70.6 ppm (downfield from internal Me_4Si), phenyl carbon signals at 91.8, 93.0, 94.1 and 114.6 ppm and the carbon monoxide ligand signal at 232.7 ppm. However, the ^{13}C NMR spectrum of the carbo-

SCHEME 1. PREPARATIVE SEQUENCE TO COMPOUND III. Correct analyses for C and H were obtained for all new compounds.



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^{a}Yield based on the amount of alcohol V used.

cation III in concentrated acid could not be obtained. When the alcohol was added to frozen, degassed, concentrated H_2SO_4 and the mixture was allowed to warm slowly, the solution became blue as the solid began to dissolve. Eventually the color changed to red and carbon monoxide was evolved. Finally, a green solution was obtained from which the alcohol V was not regenerated when it was poured into ice. When the alcohol was added to frozen, degassed CF_3CO_2H, the mixture also became blue, but a homogeneous solution did not result. Filtration gave a dilute blue solution from which a yellow solid separated* after it had stood for 2 h under nitrogen.

The preparation and isolation of III has given the first carbonium ion salt bearing an adjacent π-arenechromium tricarbonyl substituent. This salt, as our preliminary studies show, appears to be an effective intermediate in the synthesis of novel functional π-arenechromium tricarbonyl complexes. Our present studies are aimed at a further development of the chemistry of III, at the preparation of new complexes of type III with substituents on the benzene rings and at a quantitative assessment of the stabilization of carbocations of type III by NMR and other physical methods.

Acknowledgments

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*The ether formed by reaction of V with its derived carbonium ion.