METALLOTROPIC REARRANGEMENTS IN BIPHENYLCHROMIUM TRICARBONYL COMPLEXES

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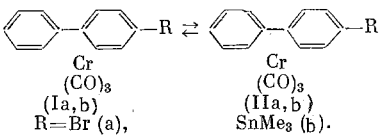
UDC 542.952.1:541.49:547.1'13:546.765

In order to study inter-ring metallotropic rearrangements such as reaction (1), we synthesized isomeric complexes (Ia), (Ib), (IIa), and (IIb). Reaction (1) was established by the redistribution of the $Cr(CO)_3$ group between the substituted and unsubstituted rings upon heating the pure isomers.



(Ia,b) R=Br (a), (IIa,b) $SnMe_3$ (b). (1)

Heating p-bromobiphenyl with $Cr(CO)_6$ at reflux in 5:1 Bu_2O_4–THF gave a 15:1 mixture of (Ia) and (IIa). The pure products were isolated by thin-layer chromatography. Heating p-trimethylstannylbiphenyl with $(NH_3)_3Cr(CO)_3$ in dioxane at 100°C gave pure (IIb). Procedures developed for the introduction of substituents into the coordinated and uncoordinated ring of naphthalenechromium tricarbonyl [1, 2] were used to obtain pure (Ib) and 2-phenyltoluenechromium tricarbonyl (III). The action of n-BuLi on (Ia) in absolute ether at −78°C and subsequent treatment of the intermediate lithium derivative (Ic, R = Li) with trimethylchlorostannane gave (Ib). Subsequent treatment of biphenylchromium tricarbonyl with n-BuLi and MeI in THF at −50°C gave (III).

The rate of isomerization of (I) depends on the nature of R and the solvent. Upon heating in Bu_2O at reflux for 12 h, (Ib) is completely and irreversibly converted to (IIb). The conversion upon heating indecane at 100°C for 7 h is 10%. Heating (IIa) in decane for 2 h gave a 5:1 mixture of (Ia) and (IIa). Under the same conditions, (III) does not isomerize.

LITERATURE CITED

1. Yu. F. Oprunenko, S. G. Malyugina, Yu. A. Ustynyuk, and N. A. Ustynyuk, Izv. Akad. Nauk SSSR, Ser. Khim., 2156 (1985).
2. Yu. F. Oprunenko, S. G. Malyugina, Yu. A. Ustynyuk, and N. A. Ustynyuk, Izv. Akad. Nauk SSSR, Ser. Khim., 2405 (1984).

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0568-5230/87/3603-0644$12.50 © 1987 Plenum Publishing Corporation