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INDUCED HALOGEN EXCHANGE IN 1,2-DICHLOROETHANE BY BIS(NN-DIETHYLDITHIOCARBAMATO)NICKEL(II)

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Summary Halogen exchange was observed when bis(NN-diethyldithiocarbamato)nickel(II), $Ni(dtc)_2$, was refluxed with excess α,α'-dibromo-o-xylene in 1,2-dichloroethane forming α,α'-dichloro-o-xylene and α,α'-bromochloro-o-xylene. This exchange is absent without $Ni(dtc)_2$ or when bis(O-ethylxanthato)nickel(II) is substituted for $Ni(dtc)_2$.

During an investigation of the ligand reaction occurring when bis(NN-diethyldithiocarbamato)nickel(II), $Ni(dtc)_2$, and excess α,α'-dibromo-o-xylene, DBX, were refluxed in 1,2-dichloroethane we observed a novel halogen exchange which was largely absent without the presence of the nickel complex. α,α'-Dichloro-o-xylene, DCX, is formed along with a small amount of α,α'-bromochloro-o-xylene, BCX.

The reaction products were conveniently separated using GLC. After refluxing the reactants for 46 hrs (exclusion of

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atmospheric moisture) the solution was filtered and an aliquot of the filtrate was used for GLC. The standards and samples were diluted with pentane. Good resolution of the halogenated products was attained by the use of a Hewlett-Packard Model 5750 gas chromatograph containing a 6 foot glass column packed with 80-100 mesh Diatoport S solid support and 3.8% silicone gum rubber UCC-W-982(methyl vinyl) liquid phase. The column temperature was 170°C, the carrier gas was a mixture of 95% argon and 5% methane. High sensitivity was achieved through the use of a Ni^{63} high temperature electron capture detector. The detection limit for DCX on introduction of 0.5µl was better than $3x10^{-7}$ molar.

In a typical reaction 2.0 g $Ni(dtc)_2$ (5.6 m mole) and 15 g DBX (57 m mole) were refluxed in 300 ml 1,2-dichloroethane. DBX underwent a 60% conversion to DCX. (DCX was also isolated in a separate experiment.) In addition, about 10% BCX was formed (estimated from the peak height ratio of BCX to DCX). In the absence of $Ni(dtc)_2$ less than 7% halogen exchange occurred. When bis(O-ethylxanthato)nickel(II), $Ni(etxn)_2$, was substituted for $Ni(dtc)_2$ in the reaction the halogen exchange was negligible. This is another example of the differing reactivity found between $Ni(dtc)_2$ and $Ni(etxn)_2$ previously pointed out by other investigators (1,2).

From the above it can be seen that DBX is consumed by the solvent 1,2-dichloroethane in the presence of the appropriate catalyst. Elder et al (3) observed a large excess of DBX

to be necessary in a synthesis conducted in this solvent. We suggest they were observing the same phenomenon and probably forming the much less reactive DCX. The only source of chlorine in this reaction is, of course, the 1,2-dichloroethane solvent. Unfortunately, we have not yet been able to tell if dibromoethane also results in this exchange.

The peach colored powder obtained as the major nickel containing product in the reaction of $Ni(dtc)_2$ and DBX in 1,2-dichloroethane at reflux will be characterized in a future publication.

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