

Reduction of (-)-Ie with $\text{NaBH}_4\text{-AlCl}_3$ to (-)-If (m.p. 95–97°, $[\alpha]^{27\text{D}} -25^\circ$ (EtOH); found: C, 62.0; H, 4.2; N, 10.3), followed by hydrogenation over Pd/C, afforded (-)-Ia (m.p. 153–158°, $[\alpha]^{26\text{D}} -49^\circ$ (EtOH)). The melting point, 232–233°, of the diacetamide, $[\alpha]^{30\text{D}} +134^\circ$ (EtOH), was undepressed by admixture of authentic⁶ diacetamide, m.p. 233–235°, $[\alpha]^{26\text{D}} +128^\circ$ (EtOH), prepared from authentic⁶ (-)-Ia, m.p. 156–158°, $[\alpha]^{24\text{D}} -47^\circ$ (EtOH), $+34^\circ$ (N HCl).⁷

(-)-Ia and (+)-DNDBCH-6-one have thus been correlated *via* (-)-Ie; (-)-Ia therefore⁴ has the S-configuration. It would appear that the assumptions underlying the theoretical treatment^{1,2} deserve re-examination.

The absolute configurations of the many common hindered biphenyls related⁸ to Ia and Ib will be listed in future publications.

(6) J. Meisenheimer and M. Höring, *Ber.*, **60**, 1425 (1927).

(7) The sign of rotation of Ia is pH dependent (F. A. McGinn, unpublished results).

(8) Cf. also K. Mislow, *Trans. N.Y. Acad. Sci.*, [2] **19**, 298 (1957).

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LEWIS ACID CHARACTER OF TELLURIUM HEXAFLUORIDE

Sir:

In a previous communication,¹ the formation of fluorotellurate salts from tellurium hexafluoride and certain alkali metal fluorides was described. We have now found that tellurium hexafluoride will react exothermally with tertiary amines to form stable adducts of the composition $\text{TeF}_6\text{-}2\text{R}_3\text{N}$. Analysis of the n-m-r data suggests that geometrical isomers are present in solutions of the trimethylamine complex.

Trimethyl- and triethylamines were added to tellurium hexafluoride in a vacuum system. The trimethylamine adduct was a white solid, but the ethyl analog had a dark color that apparently was due to minor secondary reactions. The pressure-volume relationships indicated a stoichiometry of two molecules of amine for one of the hexafluoride and analysis of the trimethylamine complex confirmed the indicated composition (*Anal.* Calcd. for $\text{TeF}_6\text{-}2\text{N}(\text{CH}_3)_3$: C, 20.0; H, 5.04; F, 31.7. Found: C, 19.56; H, 5.10; F, 29.14). Pyridine formed a complex that was highly dissociated at 25°, but amides, ethers and nitriles did not absorb tellurium hexafluoride at this temperature. This low acceptor strength and the previously cited¹ low stability of fluorotellurate salts indicate that tellurium hexafluoride is a relatively weak Lewis acid.

The F¹⁹ magnetic resonance spectrum of the molten trimethylamine adduct showed only one sharp peak; amine exchange through simple dissociation of the complex was therefore indicated. A dimethylformamide solution of the trimethylamine adduct gave a single broad resonance at 25°,

(1) E. L. Muetterties, *THIS JOURNAL*, **79**, 1004 (1957).

and at higher temperatures, the peak sharpened and shifted in the direction of the tellurium hexafluoride resonance. The amide solution was cooled to a glass that at $\sim -180^\circ$ displayed three broad resonances of approximate intensities 1:1:0.4. On warming above -180° , these three peaks broadened rapidly (but at different rates) and finally merged into a single peak. It should be noted that the weak doublet due to spin-spin coupling of fluorine with the Te¹²⁵ isotope persisted at 25° (masked at low temperatures by the broad resonances), and therefore no fluorine exchange was taking place in this system.

The n-m-r data are consistent with the behavior of an octavalent complex which has geometrical isomers and which undergoes amine exchange through simple dissociation of the complex. At $\sim -180^\circ$, the three fluorine resonances may be ascribed to the three possible isomers. On steric grounds, the two peaks of relative intensity 1 probably arise from the 1,8- and 1,3-isomers, and the peak of relative intensity 0.4 from the 1,2-isomer. Above $\sim -180^\circ$, slight dissociation of the complexes leads to amine exchange and this occurs at different rates for the three isomers. At higher temperatures the three isomers are indistinguishable in the n-m-r spectrum because of fast amine exchange. At temperatures above 25°, the complex is highly dissociated in solution and the position of resonance is a measure of the equilibrium constant for the dissociation. Without supporting data, these conclusions cannot be considered rigorously established. Unfortunately, the rapid amine exchange will not permit isolation of the postulated isomers by conventional techniques.

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A CRYSTALLIZABLE ORGANOMETALLIC COMPLEX CONTAINING TITANIUM AND ALUMINUM

Sir:

Following our previous researches¹ concerning the nature of the catalytic agent promoting the α -olefins polymerization, we have isolated a crystallizable compound containing titanium, aluminum and organometallic bonds, which causes the polymerization of ethylene.

By treating 0.01 mole of bis-(cyclopentadienyl)-titanium dichloride² suspended in 50 ml. of *n*-heptane with 0.025 mole of triethylaluminum at 70°, in the absence of air and of moisture, a slow gas evolution takes place, the titanium compound is dissolved and the solution becomes dark blue. By cooling the solution at -50° , a blue crystalline solid has been obtained in good yield.

The macroscopic blue needles of the compound, recrystallized four times from *n*-heptane, melt at 126–130° without appreciable decomposition.

(1) G. Natta, P. Pino, E. Mantica, F. Danusso, G. Mazzanti and M. Peraldo, *La Chimica e l'Industria*, **38**, 124 (1956); G. Natta, P. Pino, G. Mazzanti, U. Giannini, E. Mantica and M. Peraldo, *ibid.*, **39**, 19 (1957).

(2) G. Wilkinson and G. M. Birmigam, *THIS JOURNAL*, **76**, 4281 (1954).