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The Preparation and Reactivity of Chloroaluminum(III)toluene-3,4-dithiolate

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Treatment of dimethylaluminum chloride with toluene 3,4-dithiol, H_2TDT, affords TDTAlCl with quantitative evolution of methane. Reaction of TDTAlCl with HCl produced 2,7-dimethyl thianthrene radical cation as does the direct reaction between H_2TDT and $AlCl_3$ or $GaCl_3$. TDTAlCl was found to decompose in CH_2Cl_2 and CCl_4 while treatment with the latter followed by the former affords 5-methyl benzoditholium cation.

Introduction

The attempted synthesis of the title compound by treatment of TDTAlMe with HCl has been described, and results in alkylation of the aryl moiety whereas treatment with two equivalents affords 2,7-dimethyl thianthrene radical cation [1]. In an effort to prepare TDTAlCl, the reactivity of H_2TDT with Me_2AlCl and $AlCl_3$ was investigated.

Results

Preparation of TDTAlCl

Treatment of H_2TDT with Me_2AlCl, neat, and in the solvent systems, toluene, cyclopentane and methylcyclohexane was investigated. The neat system results in incomplete reaction based on a 65 percent yield of methane. Near quantitative evolution of methane was observed when both aromatic and aliphatic solvents were utilized, however the product in the former solvent was a pale yellow glass whereas the latter system afforded a white crystalline precipitate as summarized by eqn. 1.

$$H_2TDT + Me_2AlCl \rightarrow 2CH_4 + TDTAlCl \qquad (1)$$

Neither H_2S nor HCl were liberated during this reaction. The product, TDTAlCl, was found to be insoluble in both common aromatic and aliphatic solvents and reactive toward chlorocarbon solvents, thus limiting spectroscopic investigation to solid state infrared data – of relatively little value regarding characterization. There is little doubt that TDTAlCl is highly associated. All reported studies on TDTAlCl are for that material produced in alkanes.

Reaction of TDTAlCl with Chlorocarbons

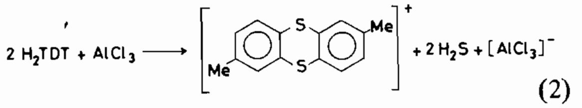
In an attempt to dissolve TDTAlCl, treatment with CH_2Cl_2 was effected with formation of a pale yellow solution which exhibited only a broad-weak ^1H NMR absorption from 2.2–2.4 ppm, in the range for the CH_3-aryl moiety. Further evidence for reaction of TDTAlCl with the solvent is the fact that after several days this solution became dark green with complete absence of the noted broad ^1H NMR absorptions while three new absorptions grew in from 2.50 to 2.78 ppm. This material was not investigated further.

Treatment of TDTAlCl with CCl_4 affords a pale brown insoluble solid. Replacement of CCl_4 by CH_2Cl_2 affords 5-methyl benzoditholium cation, $TDTCH^+$. The latter red species exhibited a ^1H NMR spectrum consisting of 3H (Me) 2.51 ppm, a multiplet 7.2–8.5 ppm and a sharp singlet, 1H (CH), at 11.10 ppm. The lit. values for the ^1H NMR absorptions of benzodithiolium cation consist of a multiplet from 7.95–8.9 ppm and a sharp singlet at 11.5 ppm [2].

Formation of 2,7-Dimethyl Thianthrene Radical Cation, I

Treatment of TDTAlCl with one equivalent of HCl results in the rapid formation of the blue oil containing I. The latter was characterized by its characteristic 9 line ESR spectrum centered at g = 2.0083, a = 1.65 gauss [3].

As an alternative method for the preparation of TDTAlCl, H_2TDT was treated with $AlCl_3$. I was again produced along with the evolution of H_2S as ideally summarized by eqn. 2.



(2)

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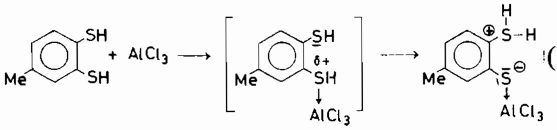
The reduced form of the oxidizing agent was not investigated.

Discussion

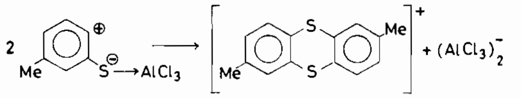
The formation of I, by treatment of H_2TDT with $AlCl_3$, is envisioned to take place as a result of intramolecular proton transfer initiated by coordination of $AlCl_3$ to S, eqn. 3,


(3)

followed by elimination of H_2S and generation of the electrophilic aryl center, eqn. 4.

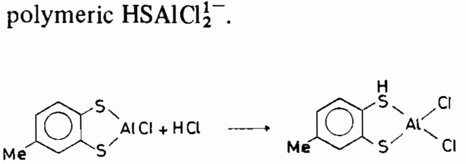

(4)

Equation 5 represents intermolecular dimerization of the generated ionic species with elimination of reduced $AlCl_3$. The formation of thianthrene radical cation


(5)

by the Lewis acid $SbCl_5$ has been described affording the binary salts of $SbCl_4^-$ and $SbCl_6^-$, with the paramagnetism of the product due entirely to thianthrene radical cation [4, 5]. The nature of the reduced aluminum chloride was not investigated further, however the observed ESR spectrum only indicated the presence of (I) with the inference being that the diamagnetic reduced oxidative state $AlCl_3$ is produced *i.e.*, $(AlCl_3^{1-})_x$.

The initial step in the formation of I, by treatment of TDTAlCl with one equivalent of HCl, is viewed as protonation of sulfur and simultaneous nucleophilic attack by Cl^- on Al, eqn. 6, followed by rearrangement to afford the ionic sulfide and $HSAlCl_2$, eqn. 7. The latter is considered the oxidizing agent towards 2,7-dimethyl thianthrene (dimerized II) with formation of I and diamagnetic–polymeric $HSAlCl_2^{1-}$.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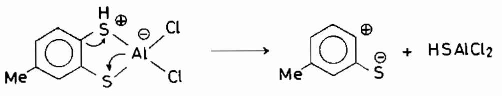
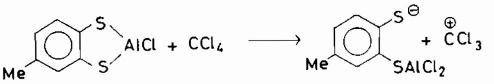
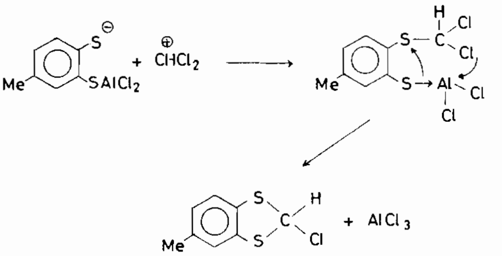

(II)
(7)

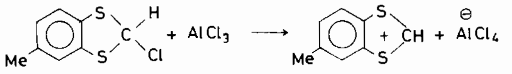
In order to produce 5-methylbenzodithiolium cation, $TDTCH^+$ (III), from TDTAlCl, it is necessary to first treat TDTAlCl with CCl_4 followed by reaction with CH_2Cl_2. The first step in the reaction mechanism is viewed as Cl^- abstraction from CCl_4, eqn. 8, and generation of IV.


(IV)
(8)

Of several alternative reaction pathways those outlined by eqns. 9–11 are favored.

$$\overset{\oplus}{C}Cl_3 + CH_2Cl_2 \rightarrow \overset{\oplus}{C}HCl_2 + HCCl_3 \qquad (9)$$


(10)


(III)
(11)

Trichloro carbonium ion abstraction of H^- from CH_2Cl_2 with generation of $CHCl_2^+$, eqn. 9, is followed by attack of the latter on sulfide and subsequent rearrangement, eqn. 10, with formation of $AlCl_3$. The final step in the chemical transformation is viewed as Cl^- abstraction by $AlCl_3$ and formation of the stable 10π electron species, III [6], eqn. 11.

Experimental

Instrumentation, experimental techniques and purification of reagents has been previously described [1].

Preparation of Me_2AlCl

Aluminumtrimethyl was treated with BCl_3 (3:1 mol ratios respectively) at –100 °C and the reaction mixture allowed to warm slowly. The complete exchange took place rapidly below room temperature affording a stoichiometric quantity of BMe_3 and Me_2AlCl. The latter was characterized by comparing its m.p., –50 °C and 25 °C vapor tension, 14 torr, with the lit. values of *ca.* –45 °C and 14.2 torr [7].

Preparation and Characterization of TDTAlCl

In a typical reaction, 1.248 g H_2TDT (8.00 mmol) was dissolved in 20 ml cyclopentane at *ca.* 0 °C and the solution slowly added to a stirred solution of 0.740 g Me_2AlCl (8.00 mmol) dissolved in 20 ml of cyclopentane at 0 °C. Methane, 15.6 mmol, was rapidly evolved and subsequently characterized. The white crystalline precipitate, TDTAlCl, exhibited i.r. (mull) absorptions at 3040(h), 2980–2980(s), 1596(s), 1470(s), 1385(s), 1260(m), 1210(m), 1185(m), 1120(s), 1038(m), 870(m), 808(s), 685(w), 615(m), 552(s), 500(s), and 448(m) cm^{-1}. TDTAlCl does not exhibit a distinct m.p. but begins to darken at *ca.* 140 °C. *Anal.* Calc. Al, 12.47; Cl, 16.36. Found: Al, 12.25; Cl, 15.65.

Reaction of TDTAlCl with HCl

The stirred solid, TDTAlCl, (5.32 mmol) was exposed to HCl gas, 5.32 mmol, at 25 °C. The HCl was rapidly absorbed affording an intense blue oil which exhibited a nine line EPR spectrum with $g = 2.0083$, $a = 1.65$ gauss.

Reaction of TDTAlCl with Chlorocarbons

Treatment of TDTAlCl, 0.1 g, with 2 ml CH_2Cl_2 at 25 °C results in the formation of a yellow solution which turns dark green in *ca.* 1 day. The initial yellow solution exhibited a ^1H NMR spectrum consisting of sharp singlets at 1.4, 4.2, 6.2 and 7.02 ppm in the *ca.* ratio 1:2:3:1 respectively, and a broad weak absorption centered at 2.3 ppm. The green solution afforded a ^1H NMR spectrum with singlets at 1.58, 2.50, and 2.62 ppm, a doublet centered at 2.78 and a broad multiplet from 7.3–8.2 ppm.

Treatment of a sample of TDTAlCl with CCl_4 produced a pale brown solid insoluble in excess CCl_4. Removal of CCl_4 followed by treatment of the brown reaction product with excess CH_2Cl_2 produced a red solution which exhibited ^1H NMR singlets at 2.40, 2.50, 2.62 and 11.10 ppm, and a broad multiplet from 7.2–8.5 ppm.

Reaction of H_2TDT with $AlCl_3$ and $GaCl_3$

H_2TDT, 0.8303 g (5.31 mmol), dissolved in cyclopentane, was added to freshly sublimed $AlCl_3$, 0.7058 g (5.31 mmol) at 25 °C. Immediately on mixing the solution became intensely blue in color. Trap to trap condensations were carried out at –40, –78, –126 and –196 °C. Pure solvent was recovered from the –78 and –126 °C traps while H_2S, 4.70 mmol, was recovered from the –196 °C trap and identified by comparison of its i.r. spectrum with that of an authentic sample. The blue oil exhibited a 9 line ESR spectrum, $g = 2.0085$, $a = 1.65$ gauss.

Identical results were obtained employing $GaCl_3$ in place of $AlCl_3$.

Acknowledgement

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