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The Chemical Reactivity of Toluene 3,4-dithiol towards Coordinated Aluminumtrimethyl

A. A. CAREY and E. P. SCHRAM

Evans Chemical Laboratory, The Ohio State University, Columbus, Ohio 43210, U.S.A.

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Treatment of $Me_3Al{\cdot}L$ (where L is NMe_3, $HNMe_2$, H_2NMe and OEt_2) with toluene 3,4-dithiol was investigated in an effort to isolate the corresponding dithiolate cyclic derivatives, $TDTAlMe{\cdot}L$. This goal was achieved where L is $HNMe_2$, whereas with NMe_3 rearrangement of the desired product took place to afford $(TDT)_3Al_2{\cdot}2NMe_3$ and $AlMe_3{\cdot}NMe_3$. In the case where L is H_2NMe, the product was polymeric. Employment of the complex with L = OEt_2 results in evolution of one or two equivalents of CH_4 with the results dependent on the solvent employed.

Introduction

We have previously reported the reaction of toluene 3,4-dithiol, H_2TDT, with aluminumtrimethyl, $AlMe_3$, [1] aluminum trichloride, $AlCl_3$, [2] and dimethylaluminum chloride, Me_2AlCl [2]. With the methylaluminum species, TDTAlMe and TDTAlCl are produced respectively, whereas $AlCl_3$ affords 2,7-dimethylthianthrene radical cation. Both TDTAlMe and TDTAlCl are highly associated as inferred by their respective insolubilities in common solvents. In an effort to produce soluble AlS_2 cyclic species, the reactivity of H_2TDT towards $AlMe_3$ adducts, $AlMe_3{\cdot}L$, was examined where L = $HNMe_2$, H_2NMe, NMe_3 and OEt_2.

Results and Discussion

Treatment of $Me_3Al{\cdot}L$ with H_2TDT was effected and the results summarized by eqn. (1). When L is $HNMe_2$, this system was investigated in the solvent

$$H_2TDT + Me_3Al{\cdot}L \rightarrow TDTAlMe{\cdot}L + 2CH_4 \qquad (1)$$

systems cyclopentane, methylcyclohexane, cyclohexane, benzene, and methylene chloride. When aliphatic solvents are utilized $TDTAlMe{\cdot}HNMe_2$, I, was produced in the form of a white crystalline precipitate. The employment of both CH_2Cl_2 and C_6H_6 resulted in yellow brown solutions of I, the ^1H NMR spectra of which change with time.

Hydrolysis of crystalline (I) is summarized by eqn. (2) and is indicative of the presence of the Me moiety

$$TDTAlMe{\cdot}HNMe_2 + 3H_2O \rightarrow CH_4 + Al(OH)_3 + \text{organic residue} \qquad (2)$$

on Al, *i.e.* evolution of CH_4. H_2TDT could not be isolated from the organic residue most likely because of its subsequent reaction with *in situ* HNR_2 [3, 4]. Hydrolysis of I was also carried out in HCl in an effort to decrease the reactivity of HNR_2 towards liberated H_2TDT, with the same results as represented by equation (2).

The infrared spectrum of $TDTAlMe{\cdot}HNMe_2$ clearly indicates the presence of νN–H at, 3200 cm^{-1}, with reference to $Me_3Al{\cdot}HNMe_2$, 3260 cm^{-1}, and the absence of νS–H found at 2533 cm^{-1} in H_2TDT. The ^1H NMR spectrum of $TDTAlMe{\cdot}HNMe_2$, at 25 °C in CH_2Cl_2, consists of singlets at 3.53 (broad), 2.35, 2.16 and –0.44 ppm in the ratios 1:6:3:3 respectively, and are assigned to *H*-N, *Me*$_2$N, *Me*-aryl and *Me*-Al respectively. At –70 the absorption centered at 2.48 ppm splits into a doublet, J HNMe = 5.1 Hz. With time $TDTAlMe{\cdot}HNMe_2$ decomposes in CH_2Cl_2 as evidenced by the fact that a new high field absorptions appears at –0.80 ppm, *Me*Al. This decomposition behavior was not observed for $HCCl_3$ solutions. The ^1H NMR abosrption at –0.80 ppm was also present in samples of $TDTAlMe{\cdot}HNMe_2$ prepared in CH_2Cl_2 and benzene, therefore the preferred method of preparation utilized alkane solvents with the reagents under high dilution.

With reference to eqn. 1, when L = OEt_2 and Et_2O is employed as the solvent only one mol CH_4 is initially liberated per mol $Me_3Al{\cdot}OEt_2$. However, during removal of OEt_2, even at –20 °C, rapid evolution of the second mol of CH_4 takes place. $TDTAlMe{\cdot}OEt_2$, II, is insoluble in Et_2O and common aromatic and aliphatic solvents. Treatment with $HCCl_3$ affords CH_4 and the ^1H NMR spectrum of the resulting solution indicates loss of complexes Et_2O from the aluminum center: Calcd. for TDTAl·

$O(C_2H_5)_2$, Me(ether)/Me(aryl) = 2, and CH_2(ether)/Me(aryl) = 1.37; found 1.3 and 0.8. (*Me* aryl, 2.22 ppm; *Me* ether, 1.15 ppm; and *CH_2* ether, 3.43 ppm).

Hydrolysis of II is summarized by eqn. (3) and resulted in formation of H_2TDT. Treatment of II

$$TDTAlMe{\cdot}OEt_2 + 3H_2O \rightarrow CH_4 + H_2TDT + OEt_2 + Al(OH)_3 \qquad (3)$$

with HCl was carried out in an effort to effect Me–Cl exchanges, *i.e.*, produce the chloroaluminum derivative, and these results are summarized by eqn. 4.

$$TDTAlMe{\cdot}OEt_2 + HCl \rightarrow TDTAlCl{\cdot}OEt_2 + CH_4 \qquad (4)$$

Furthermore, H_2TDT was recovered in high yield after hydrolysis of the reaction product, eqn. 4, indicating that alkylation of the aromatic systems did not take place during treatment of II with HCl, eqn. 4.

With reference to eqn. 1, when L = H_2NMe or NMe_3, two mol of CH_4/mol Al are liberated, however $TDTAlMe{\cdot}NMe_3$ undergoes facile rearrangement with quantitative evolution of $Me_3Al{\cdot}NMe_3$, equation 5.

$$3TDTAlMe{\cdot}NMe_3 \rightarrow Me_3Al{\cdot}NMe_3 + (TDT)_3Al_2{\cdot}2NMe_3 \qquad (5)$$

The latter was identified by comparison of its IR spectrum with an authentic sample. Furthermore, the ^1H NMR spectrum of the non-volatile reaction residue, in CH_2Cl_2, lacked a *Me*Al absorption, *ca.* –0.5 ppm; the observed absorptions are consistent with the stoichometry $(TDT)_3Al_2{\cdot}2NMe_3$, *i.e.*, N*Me* at 2.56 ppm and aryl-*Me* at 2.16 ppm in the *ca.* ratio 2:1 respectively.

When one treats initially formed $TDTAlMe{\cdot}NMe_3$ with $HCCl_3$, CH_4 is quantitatively evolved while the ^1H NMR spectrum exhibits absorptions at 2.77 ppm, N-*Me*, and 2.32 ppm, aryl *Me*, in the ratio 3:1. Previous studies have indicated that treatment of dithiolate coordinated AlMe with $HCCl_3$ results in replacement of Me by Cl [1].

With regard to $TDTAlMe{\cdot}H_2NMe$, ^1H NMR data could not be obtained because of its insolubility in non-reacting solvents, *e.g.*, treatment with CH_2Cl_2 results in immediate solution, however, a white precipitate forms within a few minutes.

Experimental

Synthetic procedures and equipment employed have been previously described as have analytical methods and purification of some solvents and starting materials [1, 2].

Reagents

Diethyl ether, Anal. Reagent, Mallinckrodt Chemical Works, was dried over phosphorus pentoxide and then lithium aluminum hydride, from which it was distilled before use. Dimethylamine, The Matheson Company, was dried over sodium and fractionated prior to use. Monomethylamine, Matheson Company, was purified like dimethyl amine. Trimethylamine, The Matheson Company, was dried over lithium aluminum hydride to remove water and dimethylamine before use. Trimethylaluminum-dimethylamine adduct, $Me_3Al{\cdot}HNMe_2$, was prepared by condensing $HNMe_2$ on an equal molar amount of $AlMe_3$ [5]. The white crystalline product exhibited a ^1H NMR spectrum in benzene with absorptions at 1.48 (*Me*N) and 1.05 (*Me*Al) in the ratio 2:3 respectively. Aluminumtrimethyltrimethylamine adduct, $Me_3Al{\cdot}NMe_3$, was prepared like the $HNMe_2$ adduct and exhibits a vapor pressure of 1 torr at 25 °C [5]. Aluminumtrimethylmonomethylamine adduct, $Me_3Al{\cdot}H_2NMe$ was prepared like the $HNMe_2$ adduct and is stable toward CH_4 evolution to 45° [6]. Aluminumtrimethyldiethylether adduct, $Me_3Al{\cdot}OEt_2$ was preapred by treating $AlMe_3$ with an equal molar quantity of OEt_2. $TDTAlMe{\cdot}HNMe_2$ was prepared by addition of H_2TDT, 0.781 g (5.01 mmol), dissolved in *ca.* 30 ml methylcyclohexane, to $AlMe_3$, 0.3600 g (5.00 mmol), dissolved in *ca.* 30 ml methylcyclohexane, over a period of several hours. Methane was continuously evolved, total = 9.9 mmol. The white crystalline precipitate was washed, *in vacuo*, with methylcyclohexane. *Anal*: Calcd. for $TDTAlMe{\cdot}HNMe_2$; Al, 11.2; CH_3 (hydrolyzable) 5.8. Found: Al, 10.9; CH_3, 5.5. IR data: 3200(m), 3020(sh), 2980(vs, nujol), 2880(vs, nujol), 2720(w), 2490(w), 1605(w), 1480(s, nujol), 1370(s, nujol), 1280(s), 1120(s), 1045(m), 995(s), 870(m,sh), 810(s), 760(m,br), 670(m,br), 590(m), 560(s), 540(sh), 520(w), and 460(w) cm^{-1}. When benzene was employed as the common solvent, near stoichiometric evolution of CH_4 was observed, however the products afforded a yellow brown solution. Solvent removal resulted in formation of a yellow-brown glass from which crystalline $TDTAlMe{\cdot}HNMe_2$ could not be recovered *via* attempted recrystallization from mixed alkane–benzene systems or from CH_2Cl_2. $TDTAlMe{\cdot}H_2NMe$ was prepared in cyclohexane analogous to that of $TDTAlMe{\cdot}HNMe_2$ to afford a white crystalline with evolution of 1.96 CH_4/Al. The product was insoluble in benzene, CCl_4 and $CHCl_3$ but initially soluble in CH_2Cl_2 affording a white precipitate within minutes. This material was not investigated further. $TDTAlMe{\cdot}NMe_3$ was prepared analogous to that of $TDTAlMe{\cdot}HNMe_2$ to afford 1.95 CH_4/Al. The white crystalline product was unstable at 25 °C affording volatile $AlMe_3{\cdot}NMe_3$ which was identified by comparison of its IR spectrum with that of an authentic sample. The non-volatile residue, $(TDT)_3Al_2{\cdot}2NMe_3$, exhibited a ^1H NMR spectrum in CH_2Cl_2 consisting of absorptions at 2.16 (*Me*-aryl) and 2.55 (*Me*N) in the ratio 1:2 respectively. IR data (nujol): 3020(vs), 2980–2920(s), 1605(m), 1470(s), 1380(s), 1290(s), 1210(m), 1115(m), 1060(s), 865(s), 810(s), 650(m), 580(s), 540(s), 475(m), and 440 cm^{-1}. TDTAlMe·NMe_3, 1.1 g (4.3 mmol) was treated with 3 *ml* $CHCl_3$ at 25 °C to afford CH_4, 4.2 mmol.

TDTAlMe·OEt_2, was prepared by addition of H_2TDT, 0.967 g (6.20 mmol), in 25 ml cyclopentane, to $AlMe_3$, 0.447 g (6.21 mmol), in 30 ml cyclopentane, to afford 11.8 mmol CH_4. TDTAlMe·OEt_2 was washed with cyclopentane to afford a pale pink glass which was insoluble in CH_2Cl_2, cyclopentane, and benzene. Reaction of TDTAlMe·OEt_2, 0.932 g (3.45 mmol) with H_2O affords 3.38 mmol CH_4 and H_2TDT which was recovered by extraction of the hydrostat in CCl_4 followed by sublimation at 25 °C, and characterization by comparison of its IR spectrum with an authentic sample, yield 0.50 g (3.2 mmol). Treatment of TDTAlMe·OEt_2, 2.45 mmol, neat with HCl gas (2.90 mmol) at 24 °C over a one week period of time affords 2.32 mmol CH_4. Hydrolysis of the residue affords no additional CH_4 while extraction of the organic residue with CCl_4 results in the isolation of H_2TDT which was identified by its IR spectrum. Attempted solution of TDTAlMe·OEt_2, 2.22 mmol in $CHCl_3$, 5 ml, results in CH_4 evolution, 2.12 mmol.

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