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THIOPHILIC REACTIONS OF 2,4,6-TRI-*t*-BUTYLPHENYLLITHIUM WITH CARBON DISULFIDE AND THIOPHOSGENE

RENJI OKAZAKI, TAKUJI FUJII, AND NAOKI INAMOTO
Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo 113, Japan

ABSTRACT

Highly sterically demanding 2,4,6-tri-*t*-butylphenyllithium (**1**) reacts with carbon disulfide to give 1,2-dibutylthio-1,2-bis(2,4,6-tri-*t*-butylphenylthio)ethene (**3**), 1-butylthio-1-(2,4,6-tri-*t*-butylphenylthio)pent-l-ene (**4**), and 2-butylthio-3-(2,4,6-tri-*t*-butylphenylthio)-1,3-dithiole-2-thione (**5**) when **1** is prepared by the reaction of 1-bromo-2,4,6-tri-*t*-butylbenzene with *n*-butyllithium. When the reaction is carried out using **1** prepared from **2** and *t*-butyllithium and then quenched with l-iodoethane, 2-ethylthio-3-(2,4,6-tri-butylphenylthio)-1,3-dithiole-2-thione and 1,2-diethylthio-1,2-bis(2,4,6–tri-*t*-butylphenylthio)ethene are produced. The formation of all these products can be explained in terms of initial thiophilic attack of **1** on the sulfur of carbon disulfide and an intermediate with a dual property of carbanion and carbene (i.e., ArSC(Li)(=S) $\rightleftharpoons$ ArS$\ddot{\mathrm{C}}$SLi) is suggested. The reaction of **1** with thiophosgene affords 1,2-dichloro-1,2-bis(2,4,6-tri-*t*-butylphenylthio)ethene, bis(2,4,6-tri-*t*-butylphenylthio)acetylene, and 1-chloro 2,4,6-tri-*t*-butylbenzene, the first two of which are explained to be formed by thiophilic attack of **1** with thiophosgene.

INTRODUCTION

In recent years much interest has been focused on the chemistry of multiple bonds containing heavier main group elements. Of such bonds the carbon-sulfur double bond has been relatively long known and extensively studied.[1]

Reactions of thiocarbonyl compounds with organometallic reagents are very unique because, unlike carbonyl compounds, the thiocarbonyl compounds often undergo thiophilic reactions in addition to normal carbophilic reactions. However, thiocarbonyl compounds so far known to undergo a thiophilic reaction are only thioketones[2,3] and thionesters.[2,4] In continuation of our work on sterically crowded thio- and selenocarbonyl compounds[5] we have undertaken a study on the reactions of 2,4,6-tri-*t*-butylphenyllithium (**1**) with other types of thiocarbonyl compounds, i.e., carbon disulfide and thiophosgene.[6].

RESULTS AND DISCUSSION

Reaction with Carbon Disulfide

The reactions of Grignard and organolithium reagents with carbon disulfide have been known

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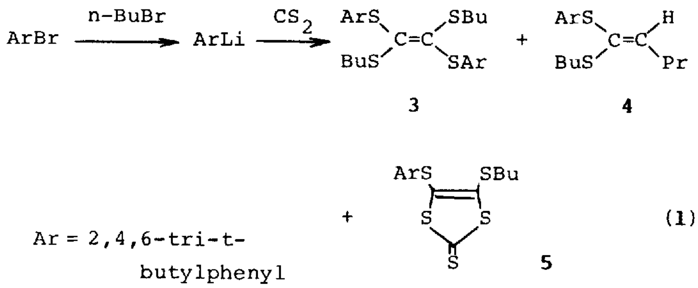
as a synthetic method for dithiocarboxylic acid derivatives and proceed via an attack on its carbon.[1,7] We have found that the reaction of sterically demanding lithium reagent **1** with carbon disulfide proceeds in a different fashion to give products derived from an attack on the sulfur atom.

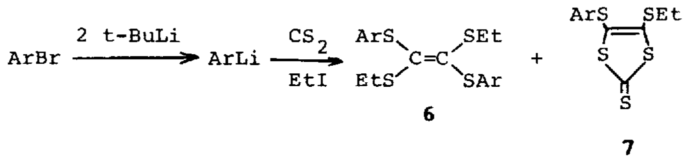
The reaction of **1**, obtained from 1-bromo-2,4,6-tri-*t*-butylbenzene (**2**) with *n*-butyllithium, with carbon disulfide in tetrahydrofuran (THF) at −78 °C resulted in the formation of **3**, **4**, and **5** in 41, 19, and 4% yields, respectively (Reaction 1). The configuration of **3** and **4** is tentatively assigned the stereochemistry indicated for steric reasons. The formation of the products containing SBu group suggests that 1-bromobutane formed in the preparation of **1** reacts with intermediates to give these final products. In order to avoid the involvement of 1-bromobutane in the reaction, **1** was prepared form **2** with 2 equiv. of *t*-butyllithium, allowed to react with carbon disulfide, and quenched with 1-iodoethane. The products thus obtained were **6** (59%) and **7** (19%) (Reaction 2). The formation of these products, **3**–**7**, can be explained only in terms of the initial thiophilic attack of **1** with carbon disulfide (Scheme 1).

The initially formed carbanion **8**, which might be equilibrated with carbene **9**, reacts with 1-bromobutane to give dithioester **10**, which undergoes alkylation again by l-bromobutane to afford **4**. The formation of **10** as an intermediate is of great interest because it suggests that umpolung of carbon disulfide reactivity is taking place in this reaction.



(1)

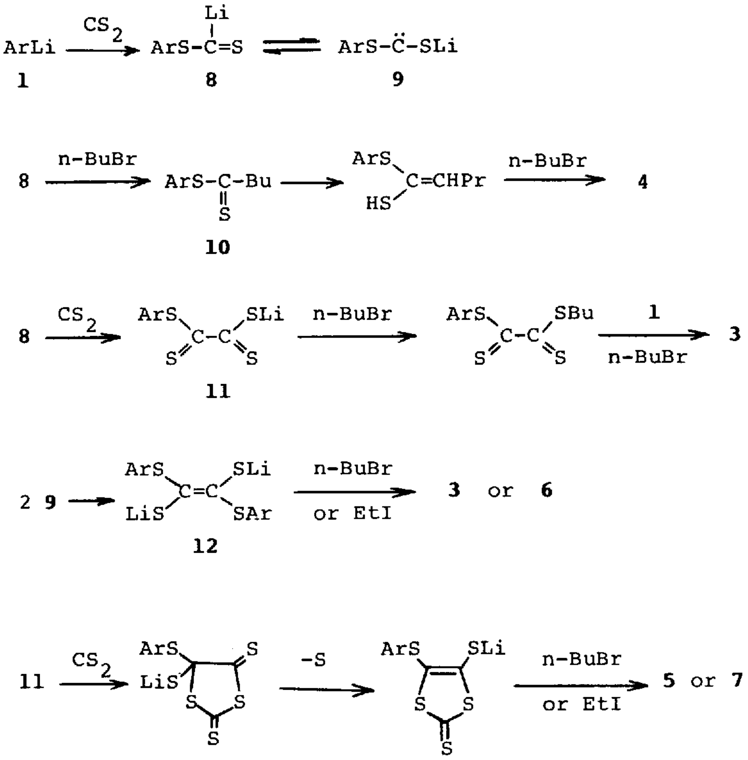
Carbanion **8** can also react with carbon disulfide to form an intermediate **11**. In Reaction 1, **11** undergoes a series of reactions with *n*-BuBr, **1**, and again *n*-BuBr to give **3**. The formation of **6** in Reaction 2 clearly suggests the intermediacy of dianion **12**. Although **12** can be formed either by dimerization of **9** or thiophilic reaction of **1** with **11**, the former route seems more likely since carbanion **1** must attack a negatively charged sulfur atom in the latter route. Similar dimerization of hetero-substituted carbenes has been reported.[8] When **11** reacts another molecule of carbon disulfide, the final product is **5** or **7**.



(2)

Although there have been a number of synthetic routes to 1,3-dithiol-2-thiones, the present approach starting with the reaction of organolithium reagents with carbon disulfide is, to our knowledge, unprecedented. This is somewhat similar, however, to the formation of 1,3-dithiole-2-thione derivatives by electrochemical or alkali metal reduction of carbon disulfide.[9]

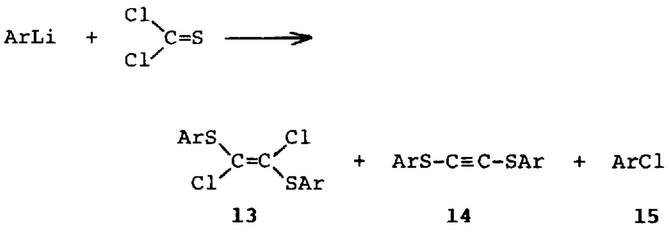
Scheme 1



In order to compare the reactivity of **1** with 2,4,6-tri-*t*-butylphenylmagnesium bromide, the Grignard reagent was reacted with carbon disulfide in refluxing THF, but no reaction took place, probably because of its intrinsic low reactivity.

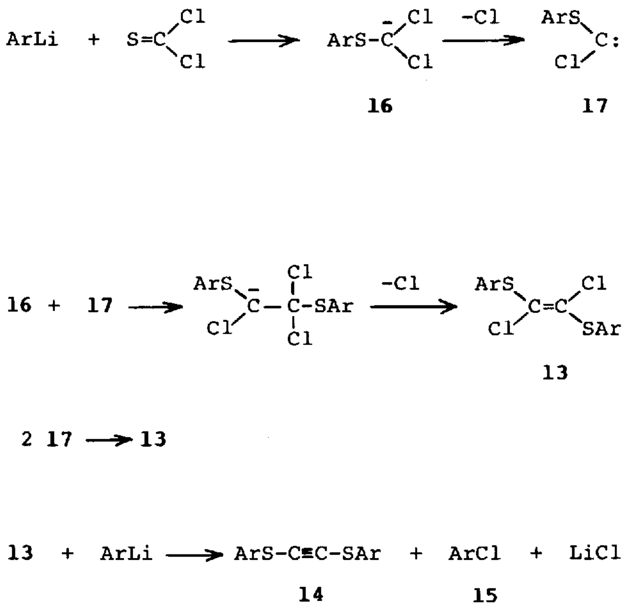
Reaction with Thiophosgen

Although there have been reported a number of reactions of thiophosgene with nucleophilic reagents, there seems no example of the reaction with organolithium or Grignard reagents.[10] When **1** prepared from **2** and *n*-butyllithium was allowed to react with thiophosgene in THF at −78 °C, compounds **13**, **14**, and **15** were formed in 7, 24, and 30% yields, respectively. The configuration of **2** was tentatively assigned *trans* for a steric reason although conclusive evidence could not be obtained experimentally.



The formation of **13** and **14** clearly indicates the involvement of the thiophilic attack of **1** on thiophosgene (Scheme 2). The reaction most likely starts with an attack of **1** on thiophosgene sulfur to give carbanion **16**, which then loses one of the chlorines affording carbene **17**. The dichloride **13** is thought to be formed either by dimerization of **17** or the reaction of **16** and **17** followed by loss of chloride ion. Acetylene **14** is probably produced by the reaction of **1** with **13**, since a separate experiment showed that **1** reacted with **13** under similar reaction conditions to afford **14** in a high yield. If the chloride **15** is formed only by this reaction of **1** with **13**, the yield of **15** should be similar to that of **14**. The fact that the yield of **15** is somewhat higher than that of **14** seems to suggest that a direct reaction of **1** with the chlorine of thiophosgene may also be operative.

Scheme 2



The reaction of 2,4,6-tri-*t*-butylphenylmagnesium bromide with thiophosgene was also carried out to give similar results; the products were **13** (17%), **14** (16%), and **15** (27%).

Conclusion

Although organolithium reagents usually react with carbon disulfide on it's carbon to give dithiocarboxylic acids, sterically crowded lithium reagent **1** undergoes a thiophilic reaction, suggesting that a steric factor plays an important role in the reaction of the organometallic reagents with thiocarbonlyl compounds. In contrast no oxophilic reaction is observed in the reaction of **1** with carbon dixodide.[11]

The present reactions represent the first example of the thiophilic reaction of organometallic reagents with carbon disulfide and thiophosgen. After our preliminary communication on the reaction of **1** with carbon disulfide,[6] Brandsma has recently reported thiophilic reactions of aryl or heteroarylpotassium with carbon disulfide.[12]

EXPERIMENTAL

Melting points are uncorrected. NMR spectra were measured with Hitachi 24B, Varian EM-390, and JEOL FX-90Q spectrometers. IR spectra were taken with a Hitachi 260–30 and mass spectra were obtained with Hitachi RMU-6 and JEOL-JMS-D300 spectrometers. Diethyl ether and THF were distilled from benzophenone ketyl under argon atmosphere just before use. All reactions were carried out under argon atmosphere.

Reaction of 2,4,6–tri-*t*-butylphenyllithium (1) with Carbon Disulfide

(a) Reaction with **1** *prepared from 1-bromo-2,4,6-tri-t-*butylbenzene *(***2***) and butyllithium*

To a THF solution (50 ml) of **1**, prepared from **2** (3·25g, 10·0 mmol)[13] and butyllithium (hexane solution, 12.0 mmol) by stirring for 10 min at −78 °C, was added carbon disulfide (0·73 ml, 12 mmol) by a syringe. The solution became red-purple at once. After being stirred for 1 h at −78 °C, the reaction mixture was allowed to be warmed to room temperature and stirred for 4 h. The solution was quenched with saturated aqueous ammonium chloride and the solvent was removed under reduced pressure. The residue was partitioned between dichloromethane and water. No appreciable amount of product could be obtained after acidification of the aqueous layer. Crude products (4·09 g) obtained from the organic layer were separated by dry column chromatography (DCC; silica gel, hexene-ether 30:1) to give 1,3,5-tri-*t*-butylbenzene[14] (0·11g, 0·45 mmol, 5%), 1,2-dibutylthio-1,2-bis(2,4,6-tri-*t*-butylphenylthio)ethene (**3**) (1·51 g, 2·05 mmol, 41%), l-butylthio-l-(2,4,6-tri-*t*-butylphenylthio)pent-l-ene (**4**) 0·48 g, 1·92 mmol, 19%), and 2-butylthio-3-(2,4,6-tri-*t*-butylphenylthio)-1,3-dithiole-2-thione (**5**) (0·81 g, 0.36 mmol, 3·6%).

3: Colorless crystals; m.p. 185·0–185·8 °C; ^{1}H-NMR(CCl_4)δ1·33(s, 18H), 1·46(s, 36H), 0·7–2·2(m, l4H), 2·35(t, J=7·5Hz, 4H), 7·31(s, 4H), ^{13}C NMR($CDCl_3$) δ13·70, 21·95, 31.34, 31·42, 32·77, 33·42, 35·00, 38·25, 122·15, 129·41, 138·13, 150·89, 156·12; MS *m/z* 756(M^+, 14%), 699(0·9), 642(17), 585(0·4), 528(6·4), 396(9·2), 364(9·2), 57(100). Analyses. Found: C, 72·78; H, 10·08; S, 16·58%. Calculated for $C_{46}H_{76}S_4$: C, 72·95; H, 10·12; S, 16·93%.

4: Yellow oil; ^{1}H-NMR(CCl_4)δ1·33(s, 9H), 1·51(s, 18H), 0·7–3·0(m, 16H), 4·06(t, J=7Hz, 1H), 7·43(s, 2H); ^{13}C NMR($CDCL_3$) δ13·49, 13·69, 21·94, 22·62, 31·32, 32·05, 32·29, 32·56, 32·62, 33·46, 38·31, 122·99, 127·24, 129·68, 134·42, 151·16, 155·71; MS *m/z* 434(m^+, 2%), 377(22), 321(20), 57(100). Analyses. Found: C, 74·81; H, 10·41; S, 14·77%. Calculated for $C_{27}H_{36}S_2$: C, 74·59; H, 10·66; S, 14·75%.

5: Deep yellow crystals; m.p. 163·8–164·5 °C; ^{1}H-NMR(CCl_4) δ1·35 (s, 9H), 1·54 (s, l8H), 0·9–3·0(m, 9H), 7·41(s, 2H); ^{13}C NMR($CDCl_3$) δ13·57, 21·70, 31·29, 31·86, 32·21, 35·38, 36·38, 38·44, 102·46, 123·53, 126·13, 129·65, 153·69, 155·57, 201·90; MS *m/z* 498(M^+, 17%), 57(100). Analyses. Found: C, 60·11; H, 8.01; S, 32·15%. Calculated for $C_{25}H_{38}S_5$: C, 60·19; H, 7·68; S, 32·13%.

(b) Reaction with **1** *prepared from* **2** *and t-butyllithium*

The solution of **1** was prepared by adding *t*-butyllithium (pentane solution, 1·4 mmol) to **2**[13] (0·203 g, 0·624 mmol) in 5 ml of THF at −78 °C and then stirred for 5 min. To this was added carbon disulfide (0·10 ml, 1·7 mmol) and the red-purple solution was stirred for 2 h at the same temperature. Ethyl iodide (0·1 ml, 1·2 mmol) was added to the solution, which was stirred for 2 h and quenched with aqueous ammonium chloride at −78 °C. A similar workup to that for (a) gave 0·254 g of crude products, which were separated by DCC (silica gel, hexane-dichloromethane 10:1) to afford 1,3,5-tri-*t*-butylbenzene[14] (0·034 g, 0·14 mmol, 22%), 2-ethylthio-3-(2,4,6-tri-*t*-butylphenylthio)-1,3-dithiole-2-thione (**6**) (0·050 g, 0·12 mmol, 19%), and 1,2-diethylthio-1,2-(2,4,6-tri-*t*-butylphenylthio)ethene (**7**) (0·13 g, 0·185 mmol, 59%).

6: Colorless crystals; m.p. 236–238 °C; ^{1}H-NMR(CCl_4)δ0·86(t, J=7·5 Hz, 6H), 1·31(s, 18H), 1·47(s, 36H), 2·35(q, J=7.5H, 4H), 7·28(s, 4H); ^{13}C NMR($CDCl_3$)δ14·00, 29·47, 31·39, 32·72, 35·08, 38·22, 122·13, 129·45, 138·47, 150·95, 156·18; MS *m/z* 700(M$^+$, 38%), 643(2), 614(38), 528(9), 57(100). Analyses. Found: C, 71·68; H, 9·62; S, 18·65%. Calculated for $C_{42}H_{68}S_4$: C, 71·94; H, 9·77; S, 18·29%.

7: Yellow oil, ^{1}H-NMR(CCl_4)δ1·16(t, J=7 Hz, 3H), 1·34(s, 9H), 1·54(s, 18H), 2·87(q, J=7 Hz, 2H), 7·39(s, 2H); MS *m/z* 420 (M$^+$, 100%), 57(57).

Reaction of 2,4,6-tri-t-butylphenylmagnesium Bromide with Carbon Disulfide

The Grignard reagent was prepared from **2** (2·63 g, 8·10 mmol) and magnesium (0·22 g, 8·91 mmol) in refluxing THF (10 ml). To this was added carbon disulfide (2·5 ml, 40 mmol) at room temperature and the solution was stirred for 2 days at room temperature and heated for 1 h under reflux. Usual workup gave 1,3,5-tri-*t*-butylbenzene[14] quantitatively.

Reaction of 1 with Thiophosgen

To a THF solution (20 ml) of **1** prepared by the reaction of **2** (0·998 g, 3·07 mmol) with butyllithium (hexane solution, 3·38 mmol) at −78 °C for 10 min was added thiophosgene[15] (0·26 ml, 3·4 mmol) by a syringe. The mixture was stirred for 50 min at −78 °C and gradually warmed to room temperature over a period of 2 h. Usual workup followed by DCC (silica gel, hexane) gave **13** (0·07 g, 0·1 mmol, 7%), **14** (0·21 g, 0·37 mmol, 24%), and **15** (0·26 g, 0·92 mmol, 30%).

13: Colorless crystals, m.p. 291·8–292·3 °C; ^{1}H-NMR(CCl_4)δ 1·33 (s, 18H), 1·48(s, 36H), 7·34(s, 4H); MS *m/z* 648(M$^+$, 8%), 57(100). Analyses. Found: C, 70·50; H, 9·12; S, 10·25%. Calculated for $C_{38}H_{58}Cl_2S_2$: C, 70·23; H, 9·00; S, 9·87%.

14: Colorless crystals, m.p. 270·0–270·2 °C; ^{1}H-NMR(CCl_4)δ1·28(s, 18H), 1·36(s, 36H), 7·23(s, 4H); ^{13}C-NMR($CDCl_3$)δ31·34, 32·35, 35·11, 38·09, 89·97, 122·88, 128·41, 150·89, 154·09; MS *m/z* 578(M$^+$, 4%), 521(7), 57(100). Analyses. Found: C, 79·08; H, 9·80; S, 11·44%. Calculated for $C_{38}H_{58}S_2$: C, 78·83; H, 10·10 S, 11·07%.

15 Was identified by comparison of its spectral data with those of an authentic sample.

Reaction of 2,4,6-tri-t-butylphenylmagnesium Bromide with Thiophosgene

The Grignard reagent was prepared from **2** (0·977 g, 3·0 mmol) and magnesium (86·0 mg, 3·54 mmol) and to this solution was added thiophosgene[15] (0·26 ml, 3.4 mmol) at room temperature. The reaction mixture was stirred for 15 h at room temperature and heated under reflux for 6 h to give a deep purple solution. Usual workup followed by DCC (silica gel, hexane) afforded **13** (0·17 g, 0·26 mmol, 17%), **14** (0·14g, 0·24 mmol, 16%), and **15** (0·23 g, 0·81 mmol, 27%).

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