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# ATTEMPTS TO POLYLITHIATE TETRABROMOARENES. THE COMPATIBILITY OF METHYL SULFATE AND BUTYLLITHIUM

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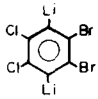
Abstract: Tetrabromo-*o*- and *p*-dichlorobenzenes are only dilithiated, even with excess *n*-butyllithium, although more than two bromines are replaced by methyl groups when such solutions are treated with methyl sulfate.

In the preceding communication[1] we described the preparation of the relatively stable 1,4-dilithioarenes 1 and 2 from tetrabromo-*o*- and *p*-dichlorobenzenes respectively. In this paper we describe efforts to replace additional bromines with lithium in these species. Trilithioarenes have presumably been obtained previously from the reaction of excess butyllithium with 1,3,5-trichloro-[2] and 1,3,5-trifluorobenzene,[3] in both cases by metalation rather than metal-halogen exchange.



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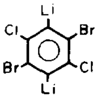

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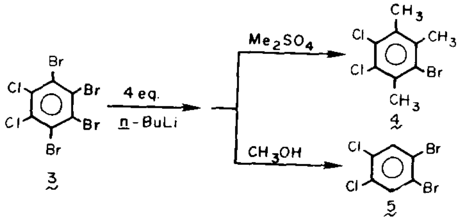
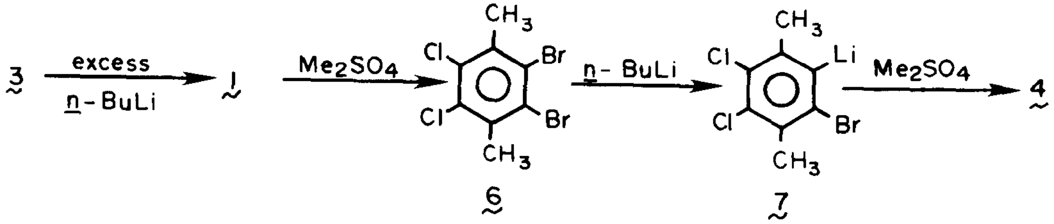
Reaction of tetrabromo-*o*-dichlorobenzene 3 with 4 eq. of *n*-BuLi (toluene, -78°C) for 4.5 h followed by quenching with methyl sulfate gave the trimethyl derivative 4 (55%).[4] This result suggested the formation of a trilithio intermediate. However, when a methanol quench was used instead of methyl sulfate, only 5 was obtained (55%); no 3,4-dichlorobromobenzene was formed. This result suggested that the intermediate was the dilithio derivative 1.



The seeming incompatibility of these results could be resolved through a sequential mechanism involving 6. This mechanism would require that (a) just prior to the addition of excess methyl sulfate the reaction mixture contains 1 and two additional equivalents of butyllithium, (b) 1 is quenched by some of the added methyl sulfate to give 6, (c) the excess methyl sulfate does not



destroy the remaining butyllithium, which can then further metalate 6 even in the presence of methyl sulfate, to give 7, (d) 7, like 1, is captured by methyl sulfate before it eliminates lithium bromide to form arynes, and (e) 4 is not further metalated under the reaction conditions, so that no o-dichlorotetramethylbenzene is formed.

That all of these conditions are likely is indicated by the following experiments. To a stirred solution of 3 containing excess methyl sulfate in toluene at -78°C was added n-butyllithium ( in separate experiments 4, 6 and 9 equivalents). A blue color developed during the addition, deepened with further addition, and faded towards the end (addition time 1.5 h). After 3 h additional stirring at -78°C, the reaction was quenched with methanol to give 4 (83-89% yield). Thus methyl sulfate and butyllithium are mutually compatible in toluene at -78°C, and all requirements in the proposed mechanism for the formation of 4 are plausible.

Methyl sulfate and butyllithium are also mutually compatible in THF at -78°C, and in this solvent all of the bromines in 3 can be replaced by methyl groups. Thus treatment of a solution of 3 (or 4) in THF containing excess methyl sulfate with excess n-BuLi at -78°C, followed by methanol quench, gave dichloroprehnitene in 95% yield. Similar treatment of tetrabromo-p-dichlorobenzene gave dichlorodurene in 89% yield. Although the bromines are replaced, the chlorines are not, even with a very large excess of n-BuLi.

We conclude that 1 and 2 cannot be further lithiated at -78°C in toluene or tetrahydrofuran, even in the presence of a large excess of n-BuLi, and that the replacement of more than two bromines with methyl groups when these solutions are treated with methyl sulfate is due to stepwise metalations and alkylations as a consequence of the mutual compatibility of methyl sulfate and n-butyllithium under the reaction conditions. Unfortunately, ethyl sulfate cannot be used similarly; intractable tars resulted.

The possibility that methyl sulfate can be used as an *in situ* trapping agent in other metalations is being explored.

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## References and Notes

1. Hart, H.; Nwokogu, G. Tetrahedron Lett. **1983**, preceding letter.
2. Gilman, H.; Haiduc, I. J. Organomet. Chem. **1968**, 12, 394.
3. Gilman, H.; Dua, S. S. J. Organomet. Chem. **1974**, 64, C1.
4. For 5: mp 215-217°C; $^1$H NMR ($CCl_4$) $\delta$ 2.43 (s, 6 H), 2.55 (s, 3 H); mass spectrum (70 eV) 268 ($M^+$, 100), 233 (36), 187 (73), 115 (64); Calcd for $C_9H_9BrCl_2$: C, 40.34; H, 3.39. Found: C, 40.30; H, 3.27.

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