

Preliminary communication

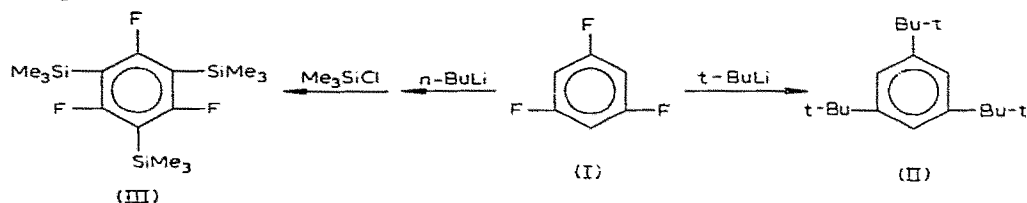
CONTRASTS BETWEEN *t*-BUTYLLITHIUM AND *n*-BUTYLLITHIUM IN SOME EXCHANGE REACTIONS

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We are reporting a striking contrast between *t*-BuLi and *n*-BuLi in some exchange reactions involving 1,3,5-trifluorobenzene (I). With *t*-BuLi, followed by treatment with chlorotrimethylsilane, all three fluorine atoms are replaced to give 1,3,5-tri-*t*-butylbenzene (II) in yields of 72%, with no apparent metalation products. With *n*-BuLi, under corresponding conditions, (I) gives predominantly 1,3,5-trifluoro-2,4,6-tris(trimethylsilyl)benzene (III) as well as products from the partial metalations: 1,3,5-trifluoro-2-trimethylsilylbenzene and 1,3,5-tri-



fluoro-2,4-bis(trimethylsilyl)benzene. The course of reaction is highly sensitive to experimental conditions, particularly temperature.

The structures of the several compounds were established by elemental analysis, spectroscopically (including ¹⁹F NMR); and by comparison with authentic specimens of (II) and of (III). We are grateful to Professor Philip C. Myhre for a sample of (II), and to Professor Nobuo Ishikawa for a specimen of (III).

The contrasts between *n*-BuLi and *t*-BuLi in some exchange reactions of *p*-difluorobenzene and of fluorobenzene show significant differences in the position and in the extent of metalation. In this connection it is interesting to note that *t*-BuLi reacts with hexafluorobenzene to give a 92% yield of 1,4-di-*t*-butyltetrafluorobenzene. However, under corresponding conditions, *n*-BuLi with hexafluorobenzene gave a mixture of *n*-butylpentafluorobenzene; 1,4-di-*n*-butyltetrafluorobenzene; 1,2,4-tri-*n*-butyltrifluorobenzene; and 1,2,4,5-tetra-*n*-butyldifluorobenzene [1,2].

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References

- 1 S.S. Dua, R.D. Howells and H. Gilman, *J. Fluorine Chem.*, 3 (1973/74) in press
- 2 For some general references, see: (a) T. Chivers, *Organometal. Chem. Revs.*, A, 6 (1970) 1; (b) I. Haiduc and H. Gilman, *Rev. Roum. Chim.*, 16 (1971) 907