

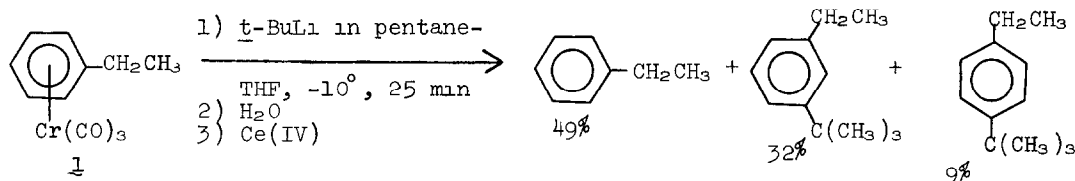
ARENE-METAL COMPLEXES. V. FACILE TERT-BUTYLATION OF ARENE-TRICARBONYLCHROMIUM(0) COMPLEXES WITH TERT-BUTYLLITHIUM<sup>1</sup>

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Treatment of (ethylbenzene)tricarbonylchromium (1) with tert-butyllithium followed by decomplexation of the arenes by oxidation gives fair yields of meta- and para-ethyl-tert-butylbenzenes. Specifically, to 50 mg (.207 mmol) of 1<sup>2</sup> in 3 ml of tetrahydrofuran was added 1 ml of ca 1.24M tert-butyllithium in pentane<sup>4</sup> at -10°. After stirring for 25 min, 2 ml of water was added. A known quantity of standard, mesitylene, was added, and the reaction mixture was extracted with ether and the extract was treated with 0.2M ceric ammonium nitrate in 50% aqueous acetonitrile. Analysis by glpc, using a 2 meter LAC 446 column at 90° showed that 49+2% ethylbenzene and 32+2% meta- and 9+2% para-ethyl-tert-butylbenzenes were produced.<sup>5</sup>



Uncomplexed arenes have been alkylated with alkyl lithium compounds but under much more forcing conditions.<sup>6</sup> For example, a 15% yield of tert-butylbenzene was obtained by heating a 1:1 mixture of benzene and tert-butyllithium in decalin at 165° for 20 hr.<sup>6,7</sup>

The reaction of tert-butyllithium and uncomplexed arenes is thought to involve the nucleophilic addition of the carbanion to the aromatic ring followed

by combination with the lithium cation to give a neutral addition product.<sup>8</sup> Other studies have indicated that the tricarbonylchromium moiety is electron withdrawing<sup>1,9</sup> and that nucleophilic attack of the complexed ring is relatively rapid.<sup>10-12</sup> The present results are thus consistent with these ideas and represent a novel nucleophilic substitution reaction of arene-tricarbonylchromium complexes in which a hydride is replaced instead of a halide ion.

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#### FOOTNOTES AND REFERENCES

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2. Prepared from ethylbenzene and hexacarbonylchromium by standard methods,<sup>3</sup> nmr (CCl<sub>4</sub>)  $\delta$  5.20(m,5), 2.48(m,2), and 1.15(m,3), mp 45-46.5° (lit.<sup>3</sup> mp 48-49°).
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4. Obtained from Foote Mineral Company.
5. Yields are averages of three runs and the products were identified by glpc retention times. The ethyl-tert-butylbenzenes were synthesized by another route and characterized by their nmr spectra and exact masses. The nmr spectrum of the product mixture was consistent with the glpc analysis.
6. J.A. Dixon and D.H. Fishman, J. Amer. Chem. Soc., **85**, 1356 (1963).
7. When ethylbenzene was treated with tert-butyllithium under our conditions, >95% of the ethylbenzene was recovered.
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