

ALKYLATION OF TRICARBONYLCYCLOHEXADIENYLIRON SALTS (1) WITH LITHIUM ALKYLs

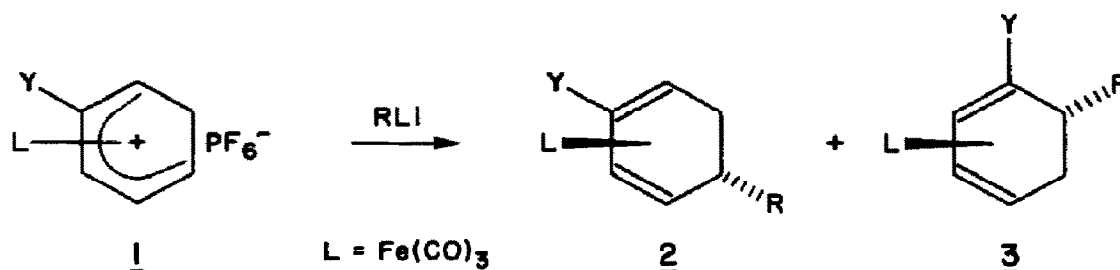
B.M. Ratnayake Bandara, Arthur J. Birch* and Thong-Chak Khor

Research School of Chemistry, Australian National University,
P.O. Box 4, Canberra, A.C.T. 2600, Australia.

SUMMARY: The salts 1 (Y=H, OMe, Me) react with RLi (R=Me, n-Bu, i-Pr, t-Bu) in CH₂Cl₂ at low temperature to give 2 and 3 in excellent yields. Nucleophilic addition at the 1-position of 1 (Y=OMe) has been observed for the first time.

Alkylation of examples of the title cations 1 has been reported with dialkylzinc,¹ dialkylcadmium^{1,2} and organocuprates.^{3,4} Alkylation with the more readily available lithium alkyls (usually the starting material for the other organometallic reagents) in ethereal solvents leads to extensive decomposition or poor yields^{4,5} (e.g. methyl lithium, 39%;⁵ t-butyl lithium, 9%⁴).

We have re-examined the reaction of 1 (Y=H, Me, OMe) with lithium alkyls and have found that the use of methylene chloride as solvent gives excellent yields of 2 and 3 (see Table). In conjunction with removal of the metal, with or without initial isomerisation of the complex, the reaction leads to potential availability of a wide range of specifically substituted cyclohexa-1,3-dienes.



With 1 (Y=Me), the addition occurred predominantly at the 5-position, in agreement with previous studies¹⁻⁴ using other alkylating reagents. However, the anticipated completely regio-selective character of 1 (Y=OMe)¹⁻⁴ was not observed with RLi (R=n-Bu, i-Pr, t-Bu) where both 2 and 3 were formed. These are the first examples of nucleophilic addition at the 1-position of 1 (Y=OMe). With t-BuLi, nucleophilic addition to the 1-position of 1 (Y=OMe) is as high as 40%. This may be due to the high reactivities of lithium alkyls in nucleophilic additions relative to organo-zinc, -cadmium or -cuprate reagents. The isomer ratio (2 and 3) in the alkylation of 1 (Y=OMe) is consistent with this factor. The same trend is not found in the case of 1 (Y=Me). This may be explicable in terms of the interplay between the reactivities of the incoming nucleophiles and that of the salts which are in the order 1 (Y=Me) > 1 (Y=OMe).⁶

TABLE*

	<u>MeLi</u>	<u>n-BuLi</u>	<u>i-PrLi</u>	<u>t-BuLi</u>
<u>1</u> (Y = H)	87% (80%) ^a	90% (90%) ^b	77% (52%) ^b	79% (69%) ^{a,d}
<u>1</u> (Y = Me)	96% (60%) ^a (75:25) ^e	96% (81%) ^b (70:30) ^e	94% (55%) ^b (90:10) ^e	87% (71%) ^a (80:20) ^e
<u>1</u> (Y = OMe)	94% (50%) ^a (100:0) ^e	84% (58%) ^b (90:10) ^e	94% (10%) ^c (90:10) ^e	87% ^f (60:40) ^e

* Isolated yields, not optimised. Spectral data are identical with those previously reported.¹⁻⁴

^a LiRCuSPh; ^b R₂Cd; ^c R₂Zn; the best yields selected from previous work.¹⁻⁴

^d Contains a very small amount of an unidentified impurity.

^e The ratio of 2 : 3; estimated from nmr spectra.

^f Satisfactory ir, mass and nmr spectra obtained.

The scope of this reaction in relation to other transition metal stabilised cations is being investigated in this laboratory.

General Procedure:

Alkyl lithium (1-1.2 eq.)⁷ was added dropwise to a stirred suspension of 1 (1 eq.) in dry CH₂Cl₂ (10 ml/mole) under nitrogen at -78°. When the yellow suspension turned to a clear or turbid solution (usually within 5-45 min), a solution of 10% aq.HCl (ca. 10 ml) was added to destroy any excess lithium alkyl. Petroleum ether (2 x vol of CH₂Cl₂) was added and the organic layer washed with water, dried (MgSO₄) and concentrated. The crude product was purified by eluting through a short column of basic alumina (grade 4) with petroleum ether. The yields of isolated products are given in the Table.

References and Notes

1. A.J. Birch and A.J. Pearson, Tetrahedron Letters, 1975, 2379.
2. A.J. Birch and A.J. Pearson, J.C.S. Perkin I, 1976, 954.
3. A.J. Pearson, Aust. J. Chem., 1976, 29, 1101.
4. A.J. Pearson, Aust. J. Chem., 1977, 30, 345.
5. A.J. Birch, P.E. Cross, J. Lewis, D.A. White and S.B. Wild, J.C.S. (A), 1968, 345.
6. 1 (Y = Me) reacts faster (ca. 5 min) with RLi than 1 (Y = OMe) (ca. 30-45 min).
7. In pentane or hexane; except for MeLi (ether).

(Received in UK 26 June 1980)