(9) L. S. Bartell and K. W. Hansen, *Inorg. Chem.*, **4**, 1777 (1965); H.-Y. Yow and L. S. Bartell, *J. Mol. Struct.*, **15**, 209 (1973).
(10) A. J. Downs and R. Schmutzler, *Spectrochim., Acta, Part A*, **23a**, 681 (1967).
(11) A. J. Downs and R. Schmutzler, *Spectrochim. Acta*, **21**, 1927 (1965).
(12) J. E. Griffiths, *J. Chem. Phys.*, **49**, 1307 (1968).
(13) A locally adapted version of the program EXCHSYS described by J. K. Kreiger, J. M. Deutsch, and G. M. Whitesides, *Inorg. Chem.*, **12**, 1535 (1973). Details of the program are given in the thesis of J. K. Kreiger, M. I. T., Cambridge Mass., 1971.
(14) J. I. Musher, *J. Chem. Educ.*, **51**, 94 (1974); J. I. Musher and W. C. Agosta, *J. Am. Chem. Soc.*, **96**, 1320 (1974).
(15) J. I. Musher, *J. Am. Chem. Soc.*, **94**, 5662 (1972).
(16) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).
(17) I. Ugi, D. Marquarding, H. Klusacek, and P. Gillespie, *Angew. Chem. Int. Ed. Engl.*, **9**, 703 (1970); I Ugi, D. Marquarding, H. Klusacek, P. Gillespie, and F. Ramirez, *Acc. Chem. Res.*, **4**, 288 (1971).
(18) K. Laidler, "Chemical Kinetics", McGraw-Hill, New York, 1950.
(19) A. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinzger, *J. Am. Chem. Soc.*, **88**, 3195 (1966); G. Binsch in "Dynamic Nuclear Magnetic Resonance Spectroscopy", L. M. Jackman and F. A. Cotton, Eds., Academic Press, New York, 1975.
(20) Alternative analyses of the rate data assuming intramolecular processes with $\Delta S^{\ddagger} = 0$ and $A = 10^{13.2}$ yielded $\Delta H^{\ddagger}$ (and $\Delta G^{\ddagger}$) values and $E_a$ values within 0.5 kcal of each other. Furthermore, the $E_a$ values are within 1 kcal of the unconstrained $\Delta G^{\ddagger}_{298}$ values; thus either may be used for comparisons.
(21) P. Meakin, E. L. Muetterties, and R. Hoffmann, *J. Am. Chem. Soc.*, **94**, 5674 (1972).
(22) R. G. Cavell and L. Vande Griend, unpublished work.
(23) (a) K. I. The and R. G. Cavell, *Inorg. Chem.*, **17**, 355 (1978); (b) *ibid.*, **16**, 1463 (1977); (c) *ibid.*, **15**, 2518 (1976); (d) *J. Chem. Soc., Chem. Commun.*, 716 (1975); (e) *ibid.*, 279 (1975); (f) D. D. Poulin and R. G. Cavell, *Inorg. Chem.* **13**, 3012 (1974); (g) *ibid.*, **13**, 2324 (1974).
(24) F. W. Bennett, H. J. Emeleus, and R. N. Haszeldine, *J. Chem. Soc.*, 1565 (1953).
(25) W. Mahler, *Inorg. Chem.*, **2**, 230 (1963).
(26) A. C. Chapman, J. Horner, D. J. Mowthorpe, and K. T. Jones, *Chem. Commun.*, 121 (1965). The chemical shift of 85% $H_3PO_4$ is +112 ppm (high field) vs. $P_4O_6$.
(27) D. Fiat, M. Halmann, L. Kugel, and J. Reuben, *J. Chem. Soc.*, 3837 (1962).
(28) This procedure was first described by S. S. Sawin, Ph.D. Thesis, University of Wisconsin, Madison, Wis., 1971.

---

Contribution from the Chemistry Department,
Oregon State University, Corvallis, Oregon 97330

# An Efficient Synthesis of Substituted Uranocenes

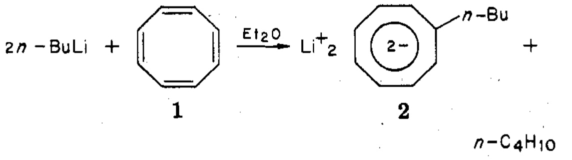
J. T. MILLER and C. W. DEKOCK*

*Received September 15, 1978*

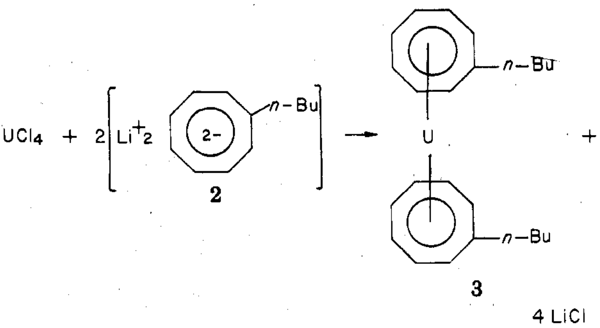
Dilithium *n*-butylcyclooctatetraenide is prepared by reaction of 2 equiv of *n*-butyllithium with 1 equiv of cyclooctatetraene in diethyl ether at 25 °C. Treatment of this solution with 0.5 equiv of $UCl_4$ dissolved in tetrahydrofuran followed by Soxhlet extraction with hexane resulted in a 50% yield of 1,1′-di-*n*-butyluranocene based on cyclooctatetraene. Treatment of 1,1′-di-*n*-butyluranocene with nitrobenzene resulted in a 51% yield of azobenzene based on cyclooctatetraene.

Grant and Streitwieser[1] have recently reported the reaction of uranocenes with aromatic and aliphatic nitro compounds to form azo compounds in good yield. They found the use of substituted uranocenes more convenient than uranocene itself due to the low solubility of the parent compound. The synthetic potential of substituted uranocenes is largely unexplored due, at least in part, to the time required for their preparation. This requires the preparation and isolation of the substituted cyclooctatetraene, reduction to the dianion, and addition of $UCl_4$ yielding the substituted uranocene. Currently, there are two methods for preparation of alkyl- or aryl-substituted cyclooctatetraenes. The procedure of Cope et al.[2] involves the addition of organolithium reagents to cyclooctatetraene, **1**, followed by refluxing and hydrolysis, to give a mixture of substituted cyclooctatetraenes and substituted cyclooctatrienes in low yield. Alternately, substituted cyclooctatetraenes may be prepared in high yield from bromocyclooctatetraene and lithium dialkylcuprate reagents.[3a,b] In this note we wish to report a simple, efficient method for the preparation of monosubstituted uranocenes.

Elsewhere we[4] have reported the preparation of the lithium alkyl- or aryl-substituted cyclooctatetraenide dianion from the reaction of **1** with organolithium reagents in diethyl ether. Treatment of **1** with 2 equiv of *n*-butyllithium in diethyl ether at 25 °C results in nearly quantitative formation of the lithium *n*-butylcyclooctatetraenide anion **2** within 1 h according to eq 1. Addition of 0.5 equiv of $UCl_4$ in tetrahydrofuran to this red solution containing **2** gave a 50% yield of 1,1′-di-*n*-butyluranocene, **3** (based on **1**), after removal of solvent and subsequent Soxhlet extraction with hexane. We have prepared other substituted uranocenes with this procedure by use of the appropriate alkyl- or aryllithium reagents in eq 1. We have found that eq 1 does not hold for lithium alkoxides or lithium dialkylamides.

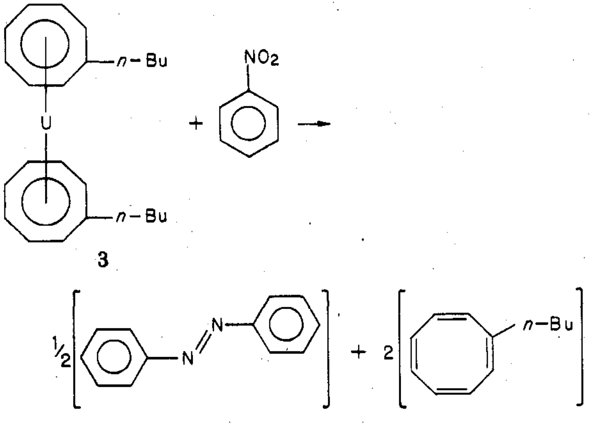


(1)



(2)

Taking advantage of this synthetic procedure, we prepared azobenzene by adding 1 equiv of nitrobenzene to the solution containing **3** according to eq 3. **3** was used without prior isolation. The reaction was instantaneous, yielding a brown



(3)

0020-1669/79/1318-1305$01.00/0 © 1979 American Chemical Society

mixture. Workup gave a 55% yield of azobenzene by VPC (based on **1**). *n*-Butylcyclooctatetraene was the only other observed product in the organic layer (by VPC and $^1H$ NMR). Streitwieser and Grant[1] report a 61% yield of azobenzene from nitrobenzene starting with isolated **3**. As Grant and Streitwieser[1] point out, this reaction is unique and is the first example of a synthetic application of uranocenes to organic chemistry. We hope our procedure stimulates the search for new uses of substituted uranocenes.

The procedure described here makes substituted uranocenes readily available from commercial reagents in minimum time. The formation of the substituted dianion in eq 1 also allows for the easy formation of other metal-substituted cyclooctatetraenides.

## Experimental Section

**General Procedure.** All air- and moisture-sensitive compounds were handled with Schlenk techniques or in a Vacuum/Atmospheres Corp. recirculating glovebox under nitrogen. Solvents were distilled or vacuum transferred from $LiAlH_4$ or sodium/benzophenone.

**1,1′-Di-*n*-butyluranocene (3).** Commercial *n*-butyllithium (2.00 M, 8.9 mL, 17.8 mmol) was added over a period of 10 min to cyclooctatetraene (**1**, 1.00 mL, 8.9 mmol) in 20 mL of diethyl ether with stirring at ambient temperature. Reaction was allowed to continue for 1 h. Completeness of reaction was monitored by VPC of **1**. Excess *n*-butyllithium does not interfere with subsequent reactions. $UCl_4$ (1.75 g, 4.5 mmol) dissolved in 25 mL of tetrahydrofuran was added dropwise to the solution at 0 °C with stirring. After the solution was stirred for 1 h, solvents were removed on the vacuum line at ambient temperature, and the green solid was transferred to a specially designed Soxhlet extractor.[5] Extraction for 4 days with hexane yielded 1.23 g (2.2 mmol, 50% yield based on **1**) of *n*-butyluranocene, **3**. Identification was made by an identical match of its infrared, NMR, mass, and visible spectra with the literature.[6]

**Nitrobenzene.** *n*-Butyluranocene, **3**, was prepared in an identical procedure as described above from 1.00 g of cyclooctatetraene (**1**, 8.9 mmol). Nitrobenzene (454 μL, 4.4 mmol) was slowly added to this solution of *n*-butyluranocene and the the solution turned immediately from green to brown. After 5 min, dilute HCl was added to the brown mixture, solids were removed by filtration, and the organic layer was analyzed by VPC for azobenzene (218 mg, 1.2 mmol, 55% yield) with an external standard. Azobenzene was identified by a match of its $^1H$ NMR and VPC retention time with those of authentic material.

**Acknowledgment.** This work was supported by grants from the National Science Foundation and the Oregon State University Research Council.

**Registry No.** 1, 629-20-9; 3, 37274-12-7; $UCl_4$, 10026-10-5; *n*-BuLi, 109-72-8; nitrobenzene, 98-95-3; azobenzene, 103-33-3.

## References and Notes

(1) C. B. Grant and A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **100**, 2433 (1978).

(2) A. C. Cope and H. O. Van Orden, *J. Am. Chem. Soc.*, **74**, 175 (1952); A. C. Cope and M. R. Kinter, *ibid.*, **73**, 3424 (1951).

(3) (a) J. Gasteigen, G. E. Gream, R. Huisgen, W. E. Konz, and U. Schnegg, *Chem. Ber.*, **104**, 2412 (1971); (b) C. A. Harmon and A. Streitwieser, *J. Org. Chem.*, **38**, 549 (1973).

(4) J. Miller, M. A. Brault, and C. W. DeKock, submitted for publication in *J. Org. Chem.*

(5) C. W. DeKock, R. S. Ely, T. E. Hopkins, and M. A. Brault, *Inorg. Chem.*, **17**, 625 (1978).

(6) A. Streitwieser, Jr., and C. A. Harmon, *Inorg. Chem.*, **12**, 1102 (1973).

---

Contribution from the School of Chemistry,
Georgia Institute of Technology, Atlanta, Georgia 30332

# Preparation and Characterization of Alkoxy(aroxy)magnesium Hydrides

E. C. ASHBY* and A. B. GOEL

*Received December 15, 1978*

A series of alkoxy- and aroxymagnesium hydrides (HMgOR, where R = Me, *i*-Pr, *t*-Bu, *t*-$BuCH_2$, $PhCH_2CH_2$, c-$C_6H_{11}$, Ph, $Ph_3C$, $Ph_2(Me)C$, 2,6-$Me_2C_6H_3$, 2,6-*i*-$Pr_2C_6H_3$, and 2,6-*t*-$Bu_2$-4-$MeC_6H_2$) has been synthesized by the redistribution of bis(alkoxy or aroxy)magnesium compounds with magnesium hydride in tetrahydrofuran. These compounds were also prepared by the reaction of magnesium hydride with the appropriate alcohol at −78 °C followed by warming the reaction mixture to room temperature. Some of the HMgOR compounds where R = $PhCH_2CH_2$, c-$C_6H_{11}$, $Ph_3C$, $Ph_2(Me)C$, 2,6-$Me_2C_6H_3$, 2,6-*i*-$Pr_2C_6H_3$, and 2,6-*t*-$Bu_2$-4-$MeC_6H_2$ were found to be THF soluble. Interestingly, THF-soluble cyclohexoxymagnesium hydrides could be prepared easily by the reduction of cyclohexanones with magnesium hydride in THF. All hydrides were characterized by elemental analysis, infrared and NMR spectroscopies, ebullioscopic molecular weight studies, X-ray powder diffraction, and vacuum DTA–TGA. Assignments of Mg–H stretching and bending modes have been made by comparison with the corresponding deuterated compounds. The products have been shown to be excellent stereoselective reducing agents toward ketones.

## Introduction

There has been considerable interest in the preparation of alkoxymetal hydrides (HMOR compounds)[1] and alkali metal alkoxymetal hydrides ($LiM(OR)_3H$, where M = B and Al).[2] Alkoxy derivatives of simple and complex metal hydrides are important as selective reducing agents in organic synthesis. Since selectivity is very much a function of the steric requirement of the reagent, alkoxy derivatives of the metal hydrides find their usefulness in that the steric requirement of the metal hydride can be varied by varying the steric requirement of the alkoxy group. In this respect, alkoxy groups can be varied in size considerably more than other substituent groups. Thus, it is well-known that lithium trimethoxyaluminohydride is a more selective reducing agent toward substituted cyclohexanones than $LiAlH_4$ itself.

Because of the interest in alkoxyaluminohydrides as selective reducing agents, we have prepared a series of sterically hindered alkoxy- and aroxymagnesium hydrides which might also function as selective reducing agents. In this connection, we have recently reported the preparation of a number of THF-soluble alkylmagnesium hydrides[3] and halogenomagnesium hydrides;[4] however, these compounds were found not to be very selective in their reduction of cyclohexanones. We have recently prepared some (dialkylamino)magnesium hydrides[5] and found that these compounds were not only soluble and stable in THF but also functioned very well as selective reducing agents toward a series cyclic ketones.[6] In view of these latter findings, we have decided to prepare a series of alkoxy- and aroxymagnesium hydrides in which the nature of the alkoxy group is varied from small (methoxy) to very large (2,6-di-*tert*-butyl-4-methylphenoxy). There is no prior art in this area except a report by Bauer[7] concerning the formation of HMgOEt which was obtained by EtMgH cleavage of $Et_2O$. Unfortunately, no evidence was provided

0020-1669/79/1318-1306$01.00/0