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THE QUANTITATIVE ESTIMATION OF LITHIUM NAPHTHALENIDE

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Summary

The concentration of lithium naphthalenide in tetrahydrofuran solution can be satisfactorily determined by a double titration method.

Lithium naphthalenide [1] has been used by Cohen [2–4] and Screttas [5,6] to prepare alkyllithiums from alkylphenyl sulphides which may not be available by conventional deprotonation. In some cases lithium 1-dimethylaminonaphthalenide [4,7–9] has been employed as an alternative reagent, but it was in connection with our use of lithium napthalenide [10] that a titration method was required.

Lithium naphthalenide is prepared from metallic lithium and naphthalene in tetrahydrofuran (THF) [5] (see Experimental section). The reaction is susceptible to many variables such as the size and quality of the lithium shot. Unlike alkyllithiums, lithium naphthalenide is a radical anion which may not act as a base [1] towards some of the usual reagents used for estimation of alkyllithiums [11]. Consequently, a double titration method was employed. The total base present was found by the addition of 1 ml of the solution under investigation to water followed by titration against standardised 0.1 *M* hydrochloric acid with phenolphthalien as indicator. The amount of base which did not arise from lithium naphthalenide was then found by quenching the reagent with methyl iodide and titrating against the hydrochloric acid after dilution with water. 1,2-Dibromomethane gave identical results to methyl iodide [5]. When the method was used to follow the concentration of lithium naphthalenide in a preparation, the titration results showed that as the concentration reached its highest level, other basic components appeared, and after prolonged reaction times the concentrations of these increased at the expense of the reagent (see Table 1), presumably, because of reaction of lithium naphthalenide with the solvent, a reaction known for alkyllithiums and THF [12]. The amount of naphthalene in solution was constant throughout the preparation; this was found by

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TABLE 1

TITRATIONS OF LITHIUM NAPHTHALENIDE IN THF vs. 0.1 *M* HYDROCHLORIC ACID

Time (h)	Run 1		Run 2	
	Total base[a] (ml 0.1 *M* acid)	Residual base[b] (ml 0.1 *M* acid)	Total base	Residual base
0	0.00	0.00	0.00	0.00
0.5	0.05	0.05		
1.0			3.30	0.35
1.25	2.20	0.65		
2.0	3.10	1.00	4.45	0.65
3.0	4.15	1.20		
4.0	–		5.35	0.80
4.25	4.85	1.30		
5.0			5.60	0.95
5.5	5.35	1.45		
7.0	5.55	1.55		
17.0			5.95	1.10
24.0	5.80	1.70		
42.0	5.97	2.05	6.10	1.51
68.0			6.05	2.40

[a] 1 ml of lithium naphthalenide in THF was added to water and the solution titrated against the acid. [b] 1 ml of lithium naphthalenide in THF was added to methyl iodide and after the addition of water the base was titrated against the acid.

taking samples at intervals, diluting them with water and then filtering off and weighing the naphthalene. When the reaction of lithium naphthalenide with methyl iodide was carried out on a preparative scale the compound isolated after extractive work-up was naphthalene. This indicates that the radical anion reacts with the methyl iodide by hydrogen abstraction rather than iodine abstraction or alkylation.

Screttas has noted that the concentration of lithium naphthalenide may be the same as the total base content, but because of the number of variables in the preparation it is recommended that the double titration method, an adaption of Gilman's [13], should be used as a check. It was noted that the optimum concentration of lithium naphthalenide can occur between two and twelve hours; this illustrated by the results of the two runs summarized in Table 1.

Experimental

Tetrahydrofuran (THF) was freshly distilled from sodium-benzophenone under nitrogen. The lithium shot employed was from Fisons. All organometallic reagents were handled under nitrogen.

Naphthalene (2.56 g, 20 mmol), lithium shot (0.14 g, 0.02 g. atoms previously washed with THF (2 × 5 ml)) and THF (50 ml) were rapidly stirred at room temperature. At intervals two aliquots (1 ml) were removed. One was added to water (10 ml) and then titrated against standardised 0.1 *M* hydrochloric acid with phenophthalien as indicator. The other was added to methyl iodide (5 ml) and after two minutes, water (10 ml) was added and the mixture was titrated against the standard acid with phenolphthalien as indicator.

Reaction of lithium naphthalenide with methyl iodide

Lithium naphthalenide prepared as described above from naphthalene (1.28 g) and lithium (0.07 g) in THF (25 ml) over 6 h was added to methyl iodide (10 ml) in THF (25 ml) at 0°C. The mixture was stirred for 1 h, poured into water (100 ml) and extracted with ether (3 × 25 ml). The extracts were washed with brine (25 ml), dried (Na_2SO_4), filtered and evaporated in vacuo to give naphthalene (1.16 g, 91%), identical with an authentic sample (m.p. TLC, NMR and IR).

References

1 N.L. Holy, Chem. Reviews, 74 (1974) 243.
2 T. Cohen, W.M. Daniewski and R.B. Weisenfeld, Tetrahedron Lett., (1978) 4665.
3 T. Cohen and R.B. Weisenfeld, J. Org. Chem., 44 (1979) 3601.
4 T. Cohen and J.R. Matz, J. Am. Chem. Soc., 102 (1980) 6900.
5 C.G. Screttas and M. Micha-Screttas, J. Org. Chem., 43 (1978) 1064.
6 C.G. Screttas and M. Micha-Screttas, J. Org. Chem., 44 (1979) 713.
7 T. Cohen and J.R. Matz, Synth. Commun., 10 (1980) 311.
8 T. Cohen and J.R. Matz, Tetrahedron Lett., 22 (1981) 2455.
9 T. Cohen, D. Ouellette, K. Pushpanado, A. Senaratne and L-C. Yu, Tetrahedron Lett., 22 (1981) 3377.
10 D.J. Ager, Tetrahedron Lett., 22 (1981) 2923.
11 See, for example, M.R. Winkle, J.M. Lansinger and R.C. Ronald, J. Chem. Soc. Chem. Commun., (1980) 87.
12 R.B. Bates, L.M. Kroposki and D.E. Potter, J. Org. Chem., 37 (1972) 560.
13 H. Gilman, F.K. Cartledge and S.-Y. Sim, J. Organometal. Chem., 1 (1963) 8.