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SINGLE-TITRATION METHOD FOR THE DETERMINATION OF LITHIUM NAPHTHALENIDE IN TETRAHYDROFURAN

CONSTANTINOS G. SCRETTAS and MARIA MICHA-SCRETTAS

Institute of Organic Chemistry, The National Hellenic Research Foundation, Athens 501/1 (Greece)

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Summary

Lithium naphthalenide in tetrahydrofuran (THF) is converted rapidly and quantitatively to the red diphenylethylene dimer dianion, $Ph_2C(Li)CH_2CH_2$-$C(Li)Ph_2$, which can be titrated against standard s-butanol in toluene.

Lithium naphthalenide in THF is becoming an increasingly useful reagent in preparative organolithium chemistry [1–3]. The reagent is prepared from lithium chips and an equivalent amount of naphthalene, and its preparation in synthetically convenient concentrations requires prolonged reaction times, 6–24 h, depending on the stirring efficiency [1]. The main use of the reagent is as a homogeneous source of lithium metal in cleaving carbon-to-heteroatom bonds, C–X, and forming the relevant C–Li reagents. This reaction has a stoicheiometry of 2/1 [4,5] i.e. it takes two molecules of $Li^+C_{10}H_8^{\cdot -}$ to give one molecule of RLi. It is therefore necessary to know the concentration of the lithium naphthalenide solution. If one prepares the reagent by employing (1) lithium metal free of surface oxides (and nitrides), (2) carefully purified THF, (3) a small excess of naphthalene to prevent formation of the corresponding dianion, which can readily cleave THF [6], and (4) ice bath temperature [6], then the observed total alkalinity of the solution should be a good measure of the lithium naphthalenide concentration, the effective alkalinity. However, it is not always possible to take these precautions, and in such a case the solution of the reagent is contaminated with impurities which may contribute to the total alkalinity of the solution, and special steps are needed to determine the effective alkalinity. In our previous studies we employed a double titration method, using ethylene bromide [4]. Recently an alternative double titration method was proposed by Ager which uses methyl iodide instead, and gives identical results with the ethylene bromide method [7]. This result was somewhat unexpected in view of the fact that alkyl halides and lithium naphthalene give alkyllithiums [8] and it seems that the methyllithium initially produced couples rapidly with excess methyl iodide.

We now report a new method of determining the concentration of $Li^+C_{10}H_8^{\cdot -}$

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TABLE 1

TITRATION RESULTS FOR DETERMINATION OF EFFECTIVE ALKALINITY OF LITHIUM NAPHTHALENIDE IN THF

Batch no. of $Li^+ C_{10}H_8^{\cdot -}$	Total alkalinity (equiv./liter) [a]	Effective alkalinity (equiv./liter) [a] by	
		Single titration	Double titration
1	1.04	0.95_5	0.96
2	1.05	0.95	0.96
3	0.91	0.81	0.82

[a] The indicated values were reproduced at least twice in three determinations.

a single titration. This method is based on the rapid and quantitative reaction of lithium naphthalenide with 1,1-diphenylethylene, according to eq.1. The dianion is intensely coloured red and it is protonated even by carbon acids, such as thiophene

$$2Li^+ C_{10}H_8^{\cdot -} + 2Ph_2C{=}CH_2 \rightarrow Ph_2C(Li)CH_2CH_2C(Li)Ph_2 + 2C_{10}H_8 \quad (1)$$

$$Ph_2C(Li)CH_2CH_2C(Li)Ph_2 + 2Bu^sOH \rightarrow Ph_2CHCH_2CH_2CHPh_2 + 2Bu^sOLi \quad (2)$$

red colourless

[4]. In the proposed method we employed s-butanol as a 0.50 *M* solution in toluene as the proton source [9], and titrated to a pale yellow end-point. This method gives results which agree to within 1% with the double titration method [4], see Table 1. Successful application of the method requires the use of pure diphenylethylene, this olefin is susceptible to autooxidation, forming benzophenone and formaldehyde, and it is necessary to keep the distilled reagent under argon in the freezing conpartment of a refrigerator. This new single titration method gives almost identical results with the double titration, but it is much faster and simpler. The proposed method does not employ reagents such as methyl iodide, which are hazardous to health.

Experimental

Aliquots and standard s-butanol solutions were handled with microsyringes of 500 μl capacity. The method of measuring the volume of the dark lithium naphthalenide solution accurately has been described previously [10]. The alcohol and the toluene used to make the 0.50 *M* s-butanol solution were freshly distilled under argon. THF was purified as described previously [1]. Diphenylethylene was prepared as previously described [11], and was distilled twice and stored under argon in the freezing compartment of a refrigerator.

Analytical procedure

A two-necked round bottom 100 ml flask equipped with a glass coated stirring bar was fitted with a rubber septum to the central neck, and connected through the side neck to an argon-vacuum line. The air inside the flask was replaced by pure argon and 0.50 ml of 1,1-diphenylethylene was introduced via a syringe. The lithium naphthalenide, 2×0.50 ml was injected from a microsyringe with a 50 mm needle directly into the diphenylethylene, avoiding contact of the solution with the flask

walls. The resulting red solution of the dianion was stirred at a moderate speed for a few seconds before titration against 0.50 *M* s-butanol in toluene to a pale yellow endpoint.

References

1 C.G. Screttas and M. Micha-Screttas, J. Org. Chem., 43 (1978) 1064.
2 C.G. Screttas and M. Micha-Screttas, J. Org. Chem., 44 (1979) 713.
3 T. Cohen, W.M. Daniewski and R.B. Weisenfeld, Tetrahedron Lett., (1978) 4665; T. Cohen and R.B. Weisenfeld, J. Org. Chem., 44 (1979) 3601; T. Cohen and J.R. Matz, J. Am. Chem. Soc., 102 (1980) 6900.
4 C.G. Screttas, J. Chem. Soc. Perkin II, (1975) 745.
5 C.G. Screttas and D.G. Georgiou, Tetrahedron Lett., (1975) 417.
6 C.G. Screttas and M. Micha-Screttas, J. Org. Chem., 48 (1983) 153.
7 D.J. Ager, J. Organomet. Chem., 241 (1983) 139.
8 C.G. Screttas, J. Chem. Soc. Chem. Commun., (1972) 752.
9 S.C. Watson and J.F. Eastham, J. Organomet. Chem., 9 (1967) 165.
10 C.G. Screttas and M. Micha-Screttas, J. Org. Chem., 46 (1981) 993.
11 C.F.H. Allen and S. Converse, Org. Synth. Coll. Vol., 1 (1941) 226.