KRATKA SAOPĆENJA SHORT COMMUNICATIONS

CCA-42 545.83:541.44:541.942:546.11

A Contribution to the Micro Determination of Active Hydrogen in Organic Compounds by Lithium Aluminium Hydride*

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Received October 12, 1956

After the discovery of lithium aluminium hydride and its remarkable reducing properties[1] it was soon evident that the reactions of $LiAlH_4$ are similar in many respects to those of Grignard reagents[2, 3]. That the more aggressive behaviour of the hydride may be useful for an analytical procedure was shown several years ago[3, 4] by replacement of the Grignard reagent in the Zerewitinoff procedure[5] for the determination of active hydrogen. There are some advantages over the classical Zerewitinoff method e. g. a more vigorous reaction and lack of many side reactions. Since then, many apparatus for active hydrogen determination following the Zerewitinoff procedure on a micro scale were used or modified for the new reagent.

Hochstein[4] used a modified Soltys apparatus[6]. Lieb and Schöniger[7] using the original Soltys apparatus, a modified reaction flask and powdered $LiAlH_4$, developed a convenient micro method for the determination of active hydrogen with lithium aluminium hydride. An electrometric titration method was also described[8]; Roth's apparatus [9] has also been used[10].

Besides the fact that in our laboratory Hochstein's modification gave very accurate results, it was of interest to investigate the possibilities for the use of the standard apparatus.

In this paper a description is given of the use of the Soltys apparatus with stock solutions of $LiAlH_4$ in n-dibutyl ether without any modification in design of the apparatus described[6] for use with Grignard's reagent. The use of a stock solution of $LiAlH_4$ has the advantage that the quantity of consumed reagent can also be determined.

Some results are reported in Table I.

EXPERIMENTAL

Reagents

A stock solution of $LiAlH_4$ was prepared by heating 0,7 g. of the powdered compound with 80 ml. of n-dibutyl ether for 20 minutes on an oil bath at 90°, allowing the mixture to cool and settle, and filtering the supernatant liquid through

* Communication No. 58 from this Laboratory

sintered glass or glass wool, directly in the reagent vessel of the Soltys apparatus, all operations being conducted under nitrogen. This yielded a solution 0,14—0,16 molar in $LiAlH_4$.

The solvents, n-dibutyl ether or N-ethylmorpholine, were dried as usual, treated with $LiAlH_4$ at 90—100° for several hours, and then distilled under reduced pressure.

Procedure

Cylinder nitrogen was used without purification other than drying over calcium chloride and phosphorus pentoxide. The test compounds were purified by the usual procedures, and with special care to exclude moisture. Solids were dried over phosphorus pentoxide at 0,01 mm. at elevated temperatures for several hours.

The weighed sample was placed in the reaction vessel of the Soltys apparatus, which was then flushed with dry nitrogen.

Other operations were identical with procedures described earlier. Special care must be given to the lubrication of the precise three-way stopcock. Good results were obtained with a silicone high vacuum grease**.

In blank determinations at 20°, 0,1—0,2 ccm. hydrogen was obtained, and 0,3—0,4 ccm. at 90°.

TABLE I

Compound	Moles $LiAlH_4$		Active hydrogen consumed		Temp. C°
	Found	Calc'd	Found	Calc'd	
Benzoic acid	1,008	1,0	0,426	0,75	17
„	0,978	1,0	0,489	0,75	17
„	0,983	1,0	0,446	0,75	18
„	1,059	1,0	0,770	0,75	95
Salicylic acid	1,878	2,0	0,728	1,0	20
Acetanilide	0,939	1,0	0,498	0,50	19
Benzanilide	0,984	1,0	0,514	0,50	20
Phenacetin	0,961	1,0	0,413	0,50	20
Benzil	0	0	0,539	0,50	19
„	0	0	0,548	0,50	18
2,5-dibenzoyl-3,4-dimethoxy-selenophene [11]	0	0	0	0,50	18
„	0	0	0,473	0,50	90
„	0	0	0,455	0,50	90
2,5-di-isobutyroyl-3,4-dihydroxy-selenophene [11]	1 169	2,0	0,555	1,0	18
„	1,937	2,0	0,916	1,0	95
2,5-di-isobutyroyl-3,4-dihydroxy-selenophene (mono-*O*-methyl) derivative	1,770	1,0	0,604	0,750	70
„	1,00	1,0	0,834	0,750	95

** The Dow Chemical Company, Midland, Michigan, U. S. A.

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IZVOD

Prilog mikro-određivanju aktivnog vodika u organskim spojevima s pomoću litijsko-aluminijskog hidrida

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Na većem je broju primjera pokazano, da Soltysov aparat za mikro-određivanje aktivnog vodika po Zerewitinoffu možemo, bez adaptacija, upotrijebiti za isto određivanje služeći se otopinama poznatoga sadržaja $LiAlH_4$ u n-butileteru.

Značajniji rezultati navedeni su u tablici I.

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ZAGREB

Primljeno 12. listopada 1956.