ACTA CHEMICA SCANDINAVICA 10 (1956) 591—593

Methoxy Substituted Naphthylmagnesium Halides and Carbon Dioxide

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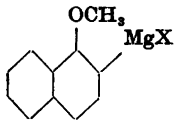
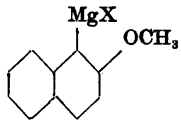
The rules for the anomalous reactivity of *o*-methoxy substituted phenylmagnesium bromides are also valid for methoxy substituted naphthylmagnesium halides, if the condensed ring is considered to be a substituent.

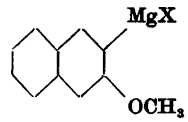
If the rules which are valid for the anomalous reactivity of *o*-methoxy substituted phenylmagnesium bromides [1] also are valid for the corresponding naphthalene derivatives, it may be expected that 1-methoxy-2-naphthylmagnesium halide (I) and 2-methoxy-1-naphthylmagnesium halide (II) will react with carbon dioxide to give only the corresponding acid, while 3-methoxy-2-naphthylmagnesium halide (III) under the same conditions will give both the corresponding acid and the corresponding ketone.



I



II



III

These predictions were fulfilled when the Grignard reagents prepared from 1-bromo-2-methoxynaphthalene, 2-iodo-1-methoxynaphthalene, and 3-iodo-2-methoxynaphthalene were allowed to react with carbon dioxide.

The iodine compounds were used since they can be more easily transformed into the corresponding Grignard reagents. The fact that different halogen compounds have been used has scarcely any significance, because the nature of the halogen does not seem to influence the anomalous reactivity. This I have found to be true in the case of *o*-methoxyphenylmagnesium bromide and *o*-methoxyphenylmagnesium iodide.

Table 1. Yields of naphthoic acids and neutral substances.

Naphthalene derivative	Acid isolated				Neutral substances g
	g	M. p.	*p*-Nitrobenzyl ester Calc. N 4.15		
			M. p.	Found N	
1-Bromo-2-methoxy-	0.84	175–176	117–118	4.25	2.35
2-Iodo-1-methoxy-	1.26	123–125	93–94	4.28	3.42
3-Iodo-2-methoxy-	1.07	131–133	123–124	4.20	2.48

EXPERIMENTAL

1-Bromo-2-methoxynaphthalene was prepared according to Franzen and Stäuble [2] through bromination of β-naphthol and methylation of the resulting 1-bromo-2-naphthol.

2-Iodo-1-methoxynaphthalene. α-Naphthylamine was nitrated and the reaction product was treated with potassium hydroxide according to Burkhardt and Wood [3]. The crude potassium 2-nitro-1-naphthoxide thus obtained was treated with methyl sulphate according to Clemo, Cockburn, and Spence [4] in order to give 2-nitro-1-methoxynaphthalene. This compound was reduced to the corresponding amine by stannous chloride in the way previously used in the synthesis of 5-amino-3-bromoveratrole [5]. The yield of 1-methoxy-2-naphthylamine after distillation under reduced pressure at 158–159°/9 mm was 71.5 %. This amine was converted into 2-iodo-1-methoxynaphthalene according to Clemo, Cockburn, and Spence. The crude product was, however, finally purified by distillation under reduced pressure. The yield of material boiling at 166–167°/10 mm and melting after recrystallization from ethyl alcohol at 41–42° was 81.4 %.

3-Iodo-2-methoxynaphthalene. 3-Hydroxy-2-naphthoic acid was successively converted into 3-methoxy-2-naphthoic acid, ethyl 3-methoxy-2-naphthoate, 3-methoxy-2-naphthoic hydrazide, ethyl 3-methoxy-2-naphthylcarbamate, and 3-methoxy-2-naphthylamine according to Jambuservala, Holt and Mason [6]. From the last mentioned substance, 3-iodo-2-methoxynaphthalene was prepared according to Clemo and Spence [7]. The yield of material boiling at 186–189°/10 mm and melting, after recrystallization from methyl alcohol, at 64.5–65.5° was 39.5 %.

The reactions between Grignard reagents and carbon dioxide were examined as has previously been described [1]. Because the halomethoxynaphthalenes used are not volatile with steam, the steam distillation was omitted. The neutral substances thus contain unreacted halomethoxy compound and perhaps methoxynaphthalenes derived from Grignard reagent that has not reacted with carbon dioxide. The results are collected in Table 1.

Only unreacted halogen compounds could be isolated from the neutral substances obtained in the experiments with Grignard reagents prepared from 1-bromo-2-methoxynaphthalene and 2-iodo-1-methoxynaphthalene. No ketone was detected.

When the neutral substances isolated from the experiment with Grignard reagent prepared from 3-iodo-2-methoxynaphthalene were treated with ether, di-3-methoxynaphthylketone was isolated. After recrystallization from ethyl alcohol, it melted at 154–155°. (Found: C 80.45; H 5.45. Calc. for $C_{23}H_{18}O_3$: C 80.68; H 5.30). Its 2,4-dinitrophenylhydrazone melted at 240–241°. (Found: N 10.87. Calc. for $C_{29}H_{22}O_6N_4$: N 10.72.)

A solution of *o*-methoxyphenylmagnesium iodide was prepared by reacting *o*-iodoanisole [8] (4.68 g) with magnesium (0.49 g) in dry ether (30 ml). Carbon dioxide was led into the solution, and when the reaction products were isolated, *o*-methoxybenzoic acid (0.55 g) and 2,2'-dimethoxybenzophenone (2.27 g) were obtained.

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Received February 2, 1956.