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Rearrangement–Cleavage of Ammonium Salts Containing a 3-Methyl-2-naphthylmethyl Group

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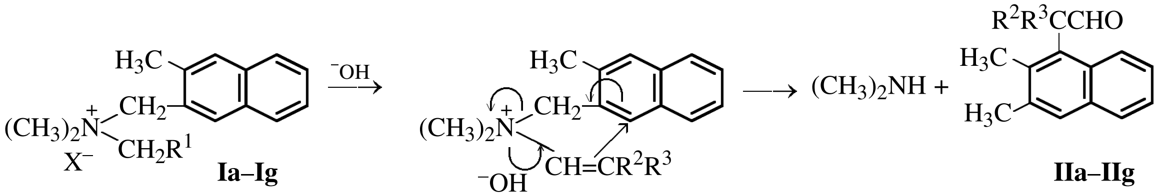
Abstract—The example of the rearrangement–cleavage under the action of 25% aqueous potassium hydroxide at 90–92°C of ammonium salts containing both 3-methyl-2-naphthylmethyl and 2-bromoethyl, allyl, methallyl, 2-bromoallyl, 3-phenylallyl, 2-propynyl, or 3-phenylphenyl-2-propynyl groups was used to show that the reaction always involves the aromatic ring of the 3-methyl-2-naphthylmethyl group. Along with rearrangement–cleavage, nucleophilic substitution of the 2-naphthylmethyl group takes place.

According to published data, ammonium salts both an α,β-unsaturated and benzyl or α-methylbenzyl groups tend to rearrangement–cleavage via a four-membered cyclic transition state [1], whereas salts with thienyl, furfuryl [2], or 1-naphthylmethyl groups [3, 4] prefer rearrangement–cleavage via a six-membered transition state because of the lower aromaticity of their rings.

Proceeding with these studies, we turned to the rearrangement–cleavage of ammonium salts **Ia**–**Ig** (Table 1) containing a 3-methyl-2-naphthylmethyl group. We suggested that these salts would undergo rearrangement–cleavage involving the aromatic ring.



Ia–Ig **IIa–IIg**

$R^1 = CH_2Br$, $R^2 = R^3 = H$ (**a**); $R^1 = CH{=}CH_2$, $R^2 = H$, $R^3 = CH_3$ (**b**); $R^1 = C(CH_3){=}CH_2$, $R^2 = R^3 = CH_3$ (**c**); $R^1 = CBr{=}CH_2$, $R^2 = Br$, $R^3 = CH_3$ (**d**); $R^1 = CH{=}CHC_6H_5$, $R^2 = H$, $R^3 = CH_2C_6H_5$ (**e**); $R^1 = C{\equiv}CH$, $R^2R^3 = {=}CH_2$ (**f**); $R^1 = C{\equiv}CC_6H_5$, $R^2R^3 = CHC_6H_5$ (**g**); X = Br (**a, b, d**–**g**), Cl (**c**).

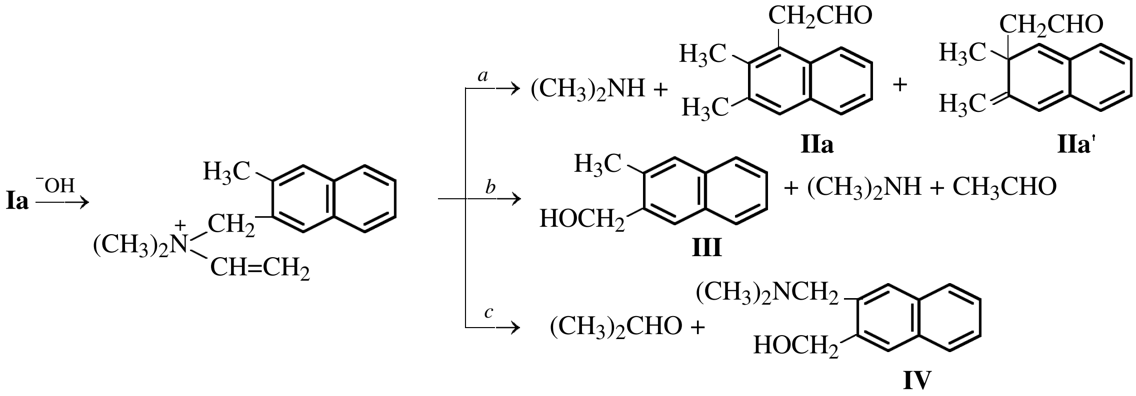
The reactions were performed by treatment of salts **Ia**–**Ig** with 25% aqueous potassium hydroxide at 90–92°C. As seen from Table 2, the reactions all gave dimethylamine and aldehydes, i.e. products of rearrangement–cleavage involving the aromatic ring, in yields of 10–40%. The lower yields of rearrangement–cleavage in this case compared with those with salts containing a 1-naphthylmethyl group [3] are probably explained by both electronic and steric factors. With salt **Ia**, along with rearrangement–cleavage products, nucleophilic substitution products, 3-methyl-2-naphthylmethyl alcohol and dimethyl(3-methyl-2-naphthylmethyl)amine were formed, implying three reaction directions (*a*, *b*, and *c*) in this case.

As seen from the scheme, acetic aldehyde can be

Table 1. Ammonium salts containing a 3-methyl-2-naphthylmethyl group

Comp. no.	Yield, %	mp, °C	R_f	*M* (titrimetrically)	
				found	calculated
Ia	95	144–145	0.43	384.5	387
Ib	98	[a]	0.54	317	320
Ic	92	[a]	0.39	292	289.5
Id	96	120–121	0.48	397.5	399
Ie	95	238–240	0.43	397	396
If	98	177–179	0.57	315	318
Ig	92	198–201	0.41	396	394

[a] Hygroscopic compound.



formed both by nucleophilic substitution of both the 3-methyl-2-naphthylmethyl and vinyl groups (*b*, *c*) of the intermediate dehydrobrominated salt. It should be noted that the IR spectra of non-nitrogenous cleavage products of salt **Ia** display, along with bands of the aromatic ring and the CHO and OH groups, a band characteristic of an *exo*-methylene group (890, 925, 985, and 1630 cm^{-1}). The ^{1}H NMR spectrum, too,

Table 2. Reactions of ammonium salts **Ia**–**Ig** with aqueous potassium hydroxide at 90–92°C

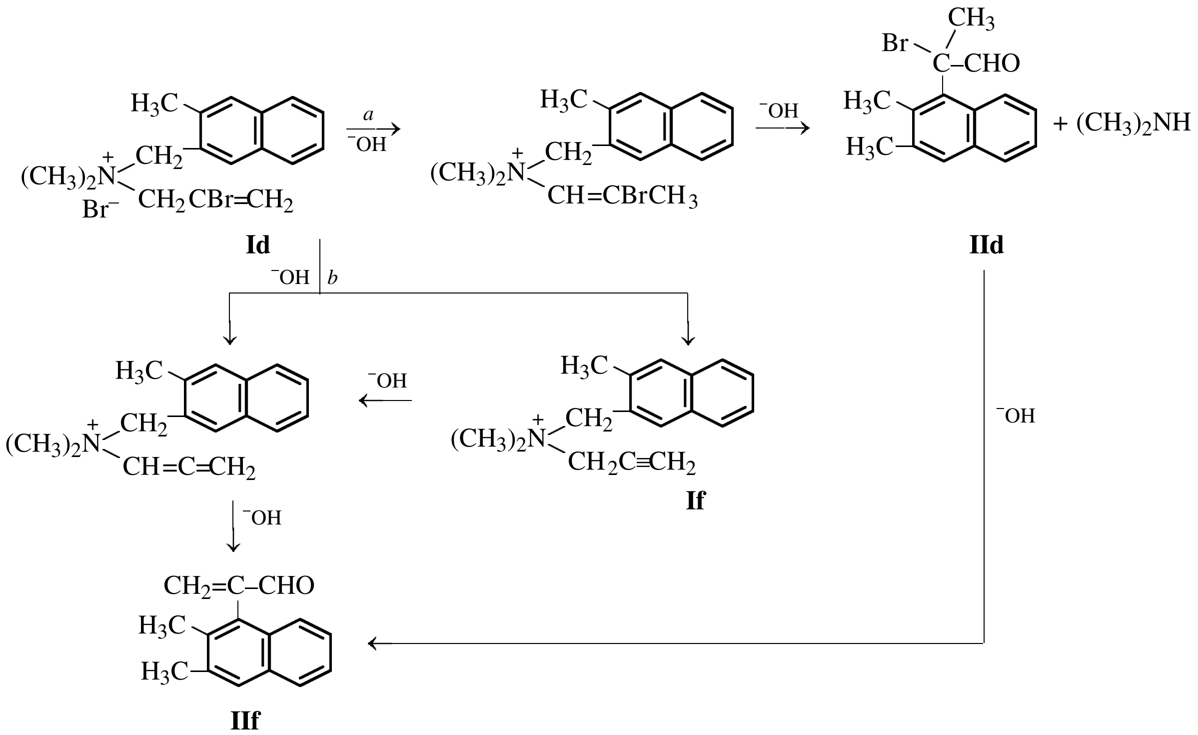
Comp. no.	Reaction products						
	amine	yield, %	non-nitrogenous	yield, %	bp, °C (*p*, mm) (mp, °C)	n_D^{20}	2,4-dinitrophenylhydrazones, mp, °C (from ethanol)
Ia	**IV**	31.7	**IIa** + **IIa'**	25.0	121–123 (2)	1.5795	111
	$(CH_3)_2NH$	37.0	**III**	28.0	(34–35)	–	–
			$CH_3CH=CHCHO$	22.8	–	–	190 [5][a]
Ib	**IV**	27.2	**IIb**	40.3	121–122 (1)	1.5838	105–106
	$(CH_3)_2NH$	64.0	**III**	14.3	(34–35)	–	–
			CH_3CH_2CHO	17.5	–	–	148–150 [6][a]
Ic	**IV**	30.7	**IIc**	34.7	142–145 (2)	1.5932	140
	$(CH_3)_2NH$	64.2	**III**	26.4	(34–35)	–	–
			$(CH_3)_2CHCHO$	26.7	–	–	168–170 [7][a]
Id	**IV**	34.8	**IId**	23.0	128–130 (1)	1.5840	102
	$(CH_3)_2NH$	40.9	**IIf**	16.6	102–104 (5)	1.5895	85–86
			$CH_2=CHCHO$	6.9	–	–	164–165 [8][a]
			Polymer[b]	28.5	–	–	
Ie	**IV**	3.4	**IIe**	19.4	[c]	–	98
	V	49.0	**III**	6.0	(34–35)	–	–
	$(CH_3)_2NH$	20.4	$C_6H_5CH_2CH_2CHO$	6.2	–	–	122–123 [9][a]
If	**IV**	68.9	**IIf**	10.2	102–104 (5)	1.5895	85–86
	$(CH_3)_2NH$	18.0	**III**	10.0	(34–35)	–	–
			$CH_2=CHCHO$	8.0	–	–	164–165 [8][a]
			Polymer[b]	~50.0	–	–	–
Ig	**IV**	19.2	**IIg**	20.1	115–117(1)	1.5898	74
	VI	39.1	**III**	15.3	(34–35)		
	$(CH_3)_2NH$[d]	22.1					

[a] The molecular weight determined by mass spectrometry fits calculated. [b] Polymeric propargyl alcohol. [c] Viscous substance. [d] Dimethyl(3-phenylpropargyl)amine was also obtained (4.8%).

provides evidence showing that both one and three naphthyl carbon atoms are involved in the reaction (Table 3), leading to formation of a mixture of aldehydes **IIa** and **IIa**'. According to these data, the mixture contains ~3–4% of aldehyde **IIa**'.

As seen from Table 2, in going from salts containing allyl (**Ib**) and methallyl (**Ic**) groups, the fraction of rearrangement–cleavage products increases (40 and 35%, respectively). However, among amine reaction products we found no dimethylallyl- and methallylamines.

The reaction of salt **Id** with alkali may occur by two direactions (*a* and *b*): Direction *a* involves no initial dehydrobromination of the 2-bromoallyl group and direction *b* involves dehydrobromination followed rearrangement–cleavage.



It is readily seen that aldehyde **IIf** can form directly from compound **IId** by dehydrobromination.

It should be noted that the contribution of dehydrobromination in the reaction of salt **Id** with triple the molar quantity of 25% aqueous potassium hydroxide reaches 73%, and, as a result, a mixture of 2-bromo-2-[1-(2,3-dimethyl)naphthyl]propanal (**IId**) and 2-[1-(2,3-dimethyl)naphthyl]acrolein (**IIf**) is formed in a total yield of 40%. The other products are dimethyl-(3-methyl-2-naphthylmethyl)amine (**IV**, 35%) and polymeric propargyl alcohol (29%). These data suggest nucleophilic substitution of the 2-propynyl group in salt **Id**.

$$\mathbf{Id} \xrightarrow{^{-}OH} \mathbf{IV} + [HOCH{=}C{=}CH_2 \longleftrightarrow HOCH_2C{\equiv}CH] \underset{\text{Polymer}}{\downarrow}$$

As would be expected, salt **If** reacts mostly by way of nucleophilic substitution of the 2-propynyl group (Table 2).

With salt **Ie**, the yields of rearrangement–cleavage and nucleophilic substitution products are low. In this case, the preferred reaction direction is Stevens rearrangement whose yield attains 49%. According to ^{1}H NMR data, the migrating group here is 3-phenylallyl. Note that of the competing [3, 2] and [1, 2] Stevens rearrangements, only the latter **Id** realized.

The same pattern is observed with salt **Ig** which contains both 3-methyl-2-naphthylmethyl and 3-phenyl-2-propynyl groups. The major reaction product here is amine **VI** formed by Stevens rearrangement with a 3-methyl-2-naphthylmethyl migrating group.

In both cases, Stevens rearrangement products **V** and **VI** were also identified by GLC using as refe-

Table 3. IR and ^{1}H NMR spectra of compounds **IIa–IIg, IIa', III, V**, and **VI**

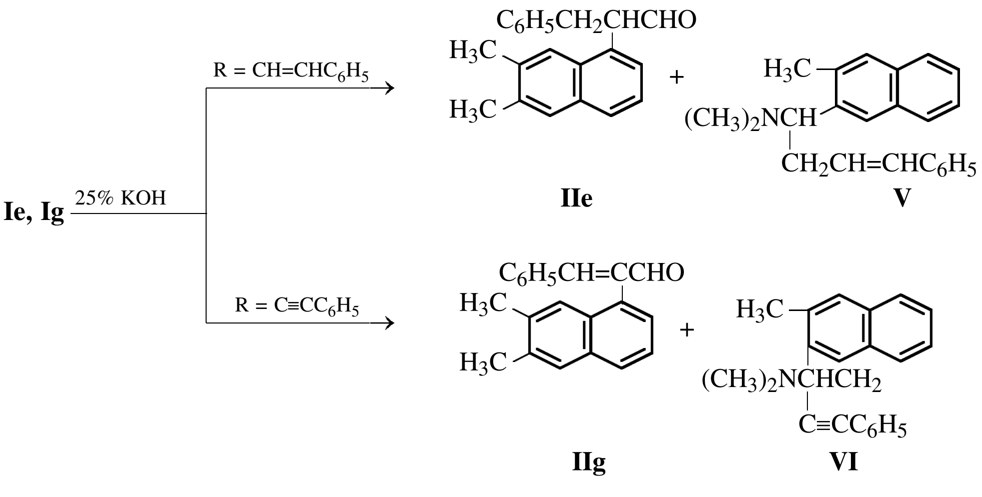
Comp. no.	IR spectrum, ν, cm^{-1}	^{1}H NMR spectrum (CCl_4), δ, ppm
IIa	780, 1510, 1590, 1905, 3060 (naphth. ring), 1715 (C=O), 2720 (CHO)	1.97 s [(6H, CH_3 (Ar)], 3.32 m (2H, $C\mathit{H}_2Ar$), 7.8–8.1 m (5H, arom. ring), 9.7 m (1H, CHO)
IIa'	890, 925, 985, 1640 (=CH_2), 705, 730, 780, 1510, 1580, 1905, 1940, 3065 (naphth. ring), 1715, 2725 (CHO)	1.97 s [3H, CH_3 (Ar)], 3.32 m (2H, $C\mathit{H}_2Ar$), 5.22 s (2H, =CH_2), 7.5–8.0 m (6H, $C_{10}H_6$), 9.7 m (1H, CHO)
IIb	760, 815, 1510, 1560, 1590, 1905, 1940, 3060 (naphth. ring), 1720, 2715 (CHO)	1.1 m (3H, $C\mathit{H}_3CH$), 1.95 s [6H, CH_3 (Ar)], 2.93 m (1H, $C\mathit{H}_3$), 7.1–8.1 m (5H, $C_{10}H_5$), 9.65 m (1H, CHO)
IIc	725, 750, 810, 1520, 1585, 1600, 1940, 3060 (naphth. ring), 1728, 2725 (CHO)	1.05 s (6H, CH_3C), 1.96 s [6H, CH_3 (Ar)], 7.0–8.12 m (5H, $C_{10}H_5$), 9,8 s (1H, CHO)
IId	570, 590 (CBr), 730, 760, 790, 1520, 1580, 1600, 3025, 3060 (naphth. ring), 1715, 2725 (CHO)	1.94 s (3H, CH_3CBr), 1.93 s [6H, CH_3 (Ar)], 7.1–7.75 m (5H, $C_{10}H_5$), 9.65 s (1H, CHO)
IIe	690, 730, 750, 1500, 1570, 1580, 1880, 1905, 1940, 3060 (naphth. ring), 1715, 2715 (CHO)	1.93 s [6H, CH_3 (Ar)], 2.42–2.85 m (3H, CH_2CH), 7.1–8.2 m (10H, C_6H_5, $C_{10}H_5$), 9.65 m (1H, CHO)
IIf	890, 1630, 3020, 3090 (CH_2=C), 720, 770, 1510, 1595, 1905, 3060 (naphth. ring), 1685, 2725 (conj. CHO)	2.00 s [6H, CH_3 (Ar)], 5.42 s (2H, CH_2=), 7.05–8.1 m (5H, $C_{10}H_5$), 9.65 s (1H, CHO)
IIg	695, 760, 1605, 1820, 1945, 3020, 3060 (naphth. ring), 1675, 2725 (conj. CHO)	1.92 s [6H, CH_3 (Ar)], 7.05 m (5H, C_6H_5), 5.80–6.2 s (1H, CH=), 7.25 m (5H, $C_{10}H_5$), 9.75 s (1H, CHO)
III	735, 780, 1520, 1590, 1905, 1940, 3060 (naphth. ring), 3400 (OH)	1.94 s [3H, CH_3 (Ar)], 4.39 s (2H, $HOC\mathit{H}_2Ar$), 7.1–8.3 m (6H, $C_{10}H_6$), 4.25 s (1H, OH)
V	700, 770, 1500, 1510, 1560, 1610, 1880, 1905, 1940, 3030, 3070 (naphth. ring), 690, 1635 (CH=CH)	2.32 s (6H, NCH_3), 1.95 s [3H, CH_3 (Ar)], 4.05 m (1H, NCH), 7.3–8.3 m (11H, C_6H_5, $C_{10}H_6$), 3.04–3.42 m (2H, $C\mathit{H}_2CH$), 5.82–6.15 m (2H, CH=)
VI	700, 750, 770, 815, 1510, 1560, 1590, 1610, 1880, 1905, 1940, 3030, 3070 (naphth. ring), 2235 (C≡C)	2.40 s (6H, NCH_3), 3.1–3.6 m (3H, $CHCH_2$), 7.2–8.2 m (11H, C_6H_5, $C_{10}H_6$), 1.94 s [3H, CH_3 (Ar)], 4.2 m (1H, NCH)

rence the authentic samples obtained Stevens rearrangements of salts **Ie** and **Ig** under the action of benzene suspensions of powdered potassium hydroxide.

The structure and composition of newly synthesized compounds were established by elemental analysis and ^{1}H NMR and IR spectroscopy (Table 3). The purity of the products was checked by GLC and TLC.

EXPERIMENTAL

The IR spectra were recorded on UR-20 and Specord IR-75 spectrometers in mineral oil or KBr pellets. The ^{1}H NMR spectra were obtained on a Perkin–Elmer R-12B spectrometer (60 MHz) in CCl_4, internal reference TMS.



Thin-layer chromatography was performed on Silufol UV-254 plates in *n*-butanol–ethanol–water–acetic acid (10 : 7 : 1 : 4), development in iodine vapor.

The mass spectra were obtained on an MKh-1320 instrument with direct inlet, ionizing voltage 70 eV.

Gas chromatography was performed on an LKhM-80 instrument with a thermal conductivity detector, column 2000 × 3 mm, 10% E-301 on Chromaton N-AW-HMDS, carrier gas helium, rate 60–80 ml/min.

The starting ammonium salts were prepared by the reactions of 1,2-dibromomethane and 2-alkenyl and 2-alkynyl bromides with dimethyl(3-methyl-2-naphthylmethyl)amine by the procedures in [10, 11] (Table 1).

Dimethyl(3-methyl-2-naphthylmethyl)amine was synthesized as described in [12].

Rearrangement–cleavage of ammonium salts Ia–Ig. A mixture of 0.015–0.02 mol of salt and 0.045–0.06 mol of 25% aqueous potassium hydroxide was heated for 5–6 h at 90–92°C in a flask equipped with a reflux condenser connected to a trap with a titrated solution of hydrochloric acid, and then treated with ether. The ether layer was separated, and the aqueous layer was treated with two portions of ether. The combined ether extracts were treated with concentrated hydrochloric acid. The ether layer was dried over magnesium sulfate and subjected to GLC analysis to determine the ratio of non-nitrogenous reaction products. Low-boiling non-nitrogenous reaction products were removed with ether and identified as 2,4-dinitrophenylhydrazones whose molecular weights were determined by mass spectrometry. The colorless semisolid material remaining after removal of ether was subjected to column chromatography on alumina (30–80 mm) in hexane–ether (8 : 1) to obtain alcohol and aldehyde. The aqueous layer was made alkaline and treated with ether to extract amine reaction products. Their ratio was determined by GLC using as references dimethyl(3-methyl-2-naphthylmethyl)- [12] and dimethyl(3- phenyl-2-propynyl)amines [13]. The amount of dimethylamine formed was determined by back titration of trap contents. The melting point of the picrate was 151°C. Mixed sample with an authentic sample showed no melting point depression.

Stevens rearrangement of ammonium salts Ie and Ig. Salt, 0.01–0.015 mol, and 0.02–0.03 mol of freshly powdered potassium hydroxide were thoroughly mixed. A weakly exothermic reaction developed. After it had been complete, 5 ml of benzene was added. The mixture was heated for 1 h on a boiling water bath with intermittent shaking, and then ether and water were added to it. The aqueous layer was treated with two portions of ether, and the ether extracts were combined and dried with magnesium sulfate. The ether was distilled off and the residue was heated in a vacuum (2 mm) for 30 min at ~50°C. After GLC analysis, the residue was distilled in a vacuum. Because of the vigorous decomposition and tarring, the rearrangement product **V** was identified without distillation. Compound **V**, viscous substance. R_f 0.43 [eluent ether–hexane (1 : 3)]. Its physicochemical characteristics coincide with those of the sample of amine **V**, obtained by the above procedure. Found, %: C 87.47; N 7.78; N 4.23. *M* 315 (by mass spectrometry). $C_{23}H_{25}N$. Calculated, %: C 87.02; H 7.94; N 4.44. *M* 315.

In a similar way, from compound **Ig** we obtained product **VI**, bp 161–162°C (1 mm), n_D^{20} 1.6105. Found, %: C 87.98; H 7.41; N 4.60. $C_{23}H_{23}N$. Calculated, %: C 88.18; H 7.35; N 4.47. By ^1H NMR and IR spectral data, the product is identical to the sample of compound **VI**, obtained by the above procedure.

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