

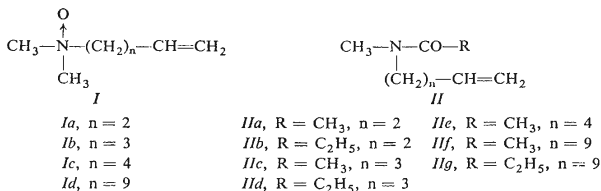
ON THE POLONOVSKI REACTION
 OF SOME DIMETHYLALKENYLAMINE N-OXIDES
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The Polonovski reaction of amine oxides with anhydrides of carboxylic acids has been studied for a relatively long period of time¹⁻¹³. Thus, *e.g.*, the reaction of dimethylalkenylamine N-oxides with acetic anhydride affords formaldehyde, the aldehyde corresponding to the alkyl group, N,N-dimethylacetamide, and N-methyl-N-alkylacetamide. Since the analogous cleavage of unsaturated amine oxides has not been mentioned so far, it appeared of interest to attempt the Polonovski reaction of the following compounds: N,N-dimethyl-3-butenylamine N-oxide (*Ia*), N,N-dimethyl-4-pentenylamine N-oxide (*Ib*), N,N-dimethyl-5-hexenylamine N-oxide (*Ic*), and N,N-dimethyl-10-undecenylamine N-oxide (*Id*).

As expected, the reaction of the derivative *Id* and acetic anhydride (propionic anhydride) led to formaldehyde, 10-undecenal, N,N-dimethylacetamide, and N-methyl-N-10-undecenylacetamide (*IIf*) as well as (with propionic anhydride) to N,N-dimethylpropionamide and N-methyl-N-10-undecenylpropionamide (*IIfg*). On the other hand, the analogous treatment of the 3-butenyl (*Ia*) and 4-pentenyl (*Ib*) derivative afforded an aldehyde with conjugated double bonds, *i.e.*, crotonaldehyde and 2-pentenal, respectively, along with formaldehyde and the corresponding



amides, namely, N,N-dimethylacetamide, N,N-dimethylpropionamide, N-methyl-N-3-butenylacetamide (*IIa*), N-methyl-N-3-butenylpropionamide (*IIb*), N-methyl-N-4-pentenylacetamide (*IIc*), N-methyl-N-4-pentenylpropionamide (*IId*). Both 2-hexenal and 5-hexenal were isolated after the reaction of acetic anhydride with the 5-hexenyl derivative *Ic*, along with N,N-dimethylacetamide and N-methyl-N-5-hexenylacetamide (*IIe*). In conclusion, the Polonovski reaction of dimethylalkenylamine N-oxides carrying lower alkenyl groups is accompanied in the case of aldehydes by migration of the double bond under the formation of a conjugated system of double bonds. With dimethyl-5-hexenylamine N-oxide, this migration occurs only to a lower extent.

EXPERIMENTAL

The melting points are uncorrected. Infrared spectra were taken on Zeiss UR-10, Perkin-Elmer 325, and MOG 2000 spectrophotometers. NMR spectra were measured on Tesla BS (80 Mc) apparatus (hexamethyldisiloxane as internal standard). The gas chromatography was effected on a Chrom 2 apparatus (140 cm column, 15% of Carbowax 20 M or 20% of Reoplex on Chromosorb).

Preparation of N,N-Dimethylalkenylamine N-Oxides

The title compounds were prepared analogously to compound *Id*. The starting amines were obtained by reported procedures¹⁴⁻¹⁶.

N,N-Dimethyl-10-undecenylamine N-oxide (Id). A stirred solution of dimethyl-10-undecenylamine¹⁶ (78 g) in methanol (280 ml) was treated in the course of 30 minutes with 28% hydrogen peroxide (120 ml). After 36 hours, the reaction was almost complete (95%), as shown by titration of the remaining amine to phenolphthalein. Excess hydrogen peroxide was destroyed by the addition of manganese dioxide or palladium on charcoal, the reaction mixture kept at room temperature for 30 minutes, and filtered. The filtrate was evaporated under diminished pressure, the residual oil dissolved in methanol, the solution dried over molecular sieves (Nalsit), and evaporated to afford 70 g (81%) of the hygroscopic N-oxide *Id*, m.p. 139°C. *N,N-Dimethyl-10-undecenylmethoxyammonium iodide*, m.p. 68°C (diethyl ether-ethanol), was prepared on keeping a mixture of the amine N-oxide *Id* and the equimolecular amount of methyl iodide at room temperature for a week. For $C_{14}H_{30}INO$ (355.3) calculated: 47.33% C, 8.51% H, 35.72% I, 3.94% N; found: 47.26% C, 8.58% H, 35.78% I, 3.95% N.

N,N-Dimethyl-3-butenylamine N-Oxide (Ia), m.p. 90°C, was converted into *N,N*-dimethyl-3-butenylmethoxyammonium iodide, m.p. 103°C. For $C_7H_{16}INO$ (257.1) calculated: 49.78% I, 5.45% N; found: 50.28% I; 5.40% N.

TABLE I

N-Methyl-N-alkenylacetamides and N-Methyl-N-alkenylpropionamides

Compound	B.p., °C/Torr	Formula (m.w.)	Calculated/Found		
			% C	% H	% N
<i>Ila</i>	93/16	$C_7H_{13}NO$ (127.2)	66.11	10.30	11.01
			65.95	10.29	10.81
<i>Ilb</i>	103/12	$C_8H_{15}NO$ (141.2)	68.04	10.71	9.92
			67.67	10.80	10.14
<i>Ilc</i>	103/16	$C_8H_{15}NO$ (141.2)	68.04	10.71	9.92
			68.19	10.69	10.24
<i>Ild</i>	113/12	$C_9H_{17}NO$ (155.3)	69.63	11.04	9.02
			69.69	10.77	8.77
<i>Ile</i>	103-106/10	$C_9H_{17}NO$ (155.3)	69.63	11.04	9.02
			69.23	11.01	8.93
<i>Ilf</i>	126/1	$C_{14}H_{27}NO$ (225.4)	74.61	12.08	6.21
			74.78	12.29	6.30
<i>Ilg</i>	136/1	$C_{15}H_{29}NO$ (239.4)	75.25	12.21	5.85
			75.27	12.11	5.96

N,N-Dimethyl-4-pentenylamine *N*-Oxide (Ib); m.p. of the crude material, 96–100°C; was converted into *N,N*-dimethyl-4-pentenylmethoxyammonium iodide, m.p. 154–156°C (ethanol–diethyl ether). For $C_8H_{18}INO$ (271.1) calculated: 5.16% N, 46.80% I; found: 5.08% N, 46.89% I.

N,N-Dimethyl-5-hexenylamine *N*-Oxide (Id), m.p. 70°C, was converted into *N,N*-dimethyl-5-hexenylmethoxyammonium iodide, m.p. 92°C (ethanol–diethyl ether). For $C_9H_{20}INO$ (285.2) calculated: 4.91% N, 44.50% I; found: 4.97% N, 44.65% I.

TABLE II

Infrared Spectra of *N*-Methyl-*N*-alkenylacetamides and *N*-Methyl-*N*-alkenylpropionamides

Compound	$\nu(C=CH_2)$	$\gamma(C=CH_2)$	δCH_3	$\nu(C=O)$	$\nu(C-H)$
<i>Ila</i>	915	995	1 470	1 655	2 930, 2 975, 3 080
<i>Ilb</i>	915	995	1 470	1 660	2 940, 2 980, 3 080
<i>Ilc^a</i>	915	995	—	1 645	2 850, 2 930, 2 990, 3 075
<i>Ild</i>	918	995	—	1 640, 1 655	2 880, 2 930, 2 980, 3 080
<i>Ile</i>	910	995	—	1 650	2 850, 2 920, 3 060
<i>Ilf</i>	910	990	1 405, 1 470	1 650	2 850, 2 930, 3 080
<i>Ilg</i>	910	990	1 430, 1 475	1 650	2 840, 2 920, 3 080

^a NMR spectrum δ : 1.95 (s) CH_3 , 2.80–2.96 (m) CH_3-N , 3.15–3.40 (m) CH_2-N , 1.40 to 1.85 (m) CH_2 , 1.85–2.20 (m) CH_2 , 4.85 (m) $CH=$, 5.55–6.05 (m) $CH_2=$.

The Reaction of Amine *N*-Oxides with Anhydrides of Carboxylic Acids

A stirred suspension of the *N*-oxide (0.2 mol) and ether (40 ml) was treated dropwise over one to three hours at 25–30°C with a solution of the anhydride (0.22 mol) in ether (40 ml). The vigorous reaction was accompanied by darkening. The reaction mixture was stirred at room temperature for additional 12 hours and then decomposed under cooling with saturated aqueous sodium hydrogen carbonate. The aqueous layer was separated and extracted with ether and then with chloroform. The organic layers were combined, dried over sodium sulfate, evaporated, and the residue distilled through a Vigreux column. As shown by gas chromatography, the fractions were not homogeneous. The additional purification was performed on a column of alumina (Brockmann activity IV). The pure amides were subjected to elemental analysis (Table I), measurement of infrared spectra (Table II), and compared with authentic specimens (*N,N*-dimethylacetamide and *N,N*-dimethylpropionamide). The formaldehyde was determined polarographically¹⁷. Crotonaldehyde¹⁸, 2-pentenal¹⁹, 2-hexenal²⁰, 5-hexenal²¹, and 10-undecenal²² were converted to the reported 2,4-dinitrophenylhydrazones. The isomeric hexenals, 2- and 5-hexenal, were separated in the form of 2,4-dinitrophenylhydrazones by chromatography on a column of alumina (Brockmann activity III). The course of column chromatography was checked by thin-layer chromatography on silica gel (Silufol sheets). Crotonaldehyde obtained in the reaction of the *N*-oxide *Ia* was also determined by gas chromatography on comparison with an authentic specimen. 2-Pentenal was also determined as semicarbazone²³.

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