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EPOXIDATION OF PROPYL- AND ISOBUTYL-β-ALKYLVINYLKETONES

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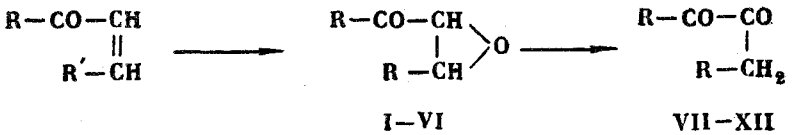
A study is made of the epoxidation of hepten-2-one-4, octen-3-one-5, nonen-4-one-6, 2-methylhepten-5-one-4, 2-methyloctene-5-one-4, and 2-methylnonen-5-one-4 with alkaline methanolic hydrogen peroxide. 46-71% yield of the corresponding epoxy ketones are obtained. It is shown that treatment of the 2, 3-epoxyheptanone-4, 3, 4-epoxyoctanone-5, 4, 5-epoxynonanone-6, 2-methyl-5, 6-epoxyheptanone-4, 2-methyl-5, 6-epoxyoctanone-4 and 2-methyl-5, 6-epoxynonanone-4 with zinc chloride isomerizes them to, respectively, heptandione-3, 4, octandione-4, 5, nonandione-4, 5, 2-methylheptandione-4, 5, 2-methyloctandione-4, 5, and 2-methylnonandione-4, 5 in upto 78% yield.

In recent papers [1, 2] it was shown that higher alkylideneacetones and branched chain α, β unsaturated aliphatic ketones gave good yield of the corresponding epoxy ketones when oxidized with alkaline hydrogen peroxide. It was of interest to investigate epoxidation of some propyl- and isobutyl-β-alkylvinylketones by that method, in connection with this kind of reactivity, and also with a view to accumulating relevant data. In the present work the action of methanolic alkaline hydrogen peroxide, with cooling, on hepten-2-one-4, octen-3-one-5, nonen-4-one-6, 2-methylhepten-5-one-4, 2-methyloctene-5-one-4, and 2-methylnonen-5-one-4 gives the corresponding epoxyketones I-IV in up to 71% yields. Distillation of these epoxy ketones with catalytic amounts of zinc chloride gives rise to smooth rearrangement of the C—O bond of an epoxy group, resulting in formation of the α-diketones VII-XII. The simplicity of the method, and the good yield of the resultant diketones makes it of practical interest for preparing these compounds, which are often accessible only with difficulty.



I—VI VII—XII

$R = C_3H_7$, $i\text{-}C_4H_9$; $R' = CH_3$, C_2H_5, C_3H_7.

The boiling points of diketones VII-XII (heptandione-3, 4, $R = C_3H_7$, $R' = CH_3$, octandione-4, 5, $R' = C_3H_7$, $R' = C_2H_5$, and nonandione-4, 5, $R = R' = C_3H_7$) as well as the melting points of their dioximes, are the same as, or very close to, those given in the literature for the same compounds synthesized by other methods [4, 5, 6]. General properties and the epoxyketones and diketones prepared are given in Table 1.

Experimental

The starting propyl-and isobutyl-β-alkylvinylketones were prepared by reacting propyl-and isobutyl-β-dimethylaminovinylketones [7] with the appropriate magnesium alkyl halides [8]. Hepten-2-one-4 had bp 74-75°(12 mm), n_D^{22} 1.4463; octen-3-one-5, bp 83-85° (32 mm), n_D^{20} 1.4459; nonen-4-one-6, bp 100-102° (25 mm), 183-187° (740 mm), n_D^{21} 1.4435, 2-methylhepten-5-one-4, bp 49-50° (5 mm), n_D^{25} 1.4370, 2-methyloctene-5-one-4, bp 83-85° (22 mm), n_D^{20} 1.4392; and 2-methylnonen-5-one-4, bp 105-107°(25 mm), n_D^{20} 1.4450, agreeing with the literature data [8-13]. The ketones were epoxidized in the same way [1]. Epoxy groups in the resultant epoxy ketones were determined by titration with ethereal hydrogen chloride [14]. The epoxide value thus found was generally about 1. Epoxyketones I-VI were isomerized to α-diketones VII-XII by heating with anhydrous zinc chloride. To the epoxyketone was added 2-2.5% of its own weight of anhydrous zinc chloride, and it was then slowly distilled from a small flask; the crude product was dried over calcined potassium carbonate, and then repeatedly distilled under reduced pressure or at atmospheric pressure. The epoxyketones were colorless, rather mobile liquids with a characteristic pleasant odor, soluble with difficulty in water, readily soluble in organic solvents. The α-diketones were oily, fragrant, yellowish-green substances. The 2, 4-dinitrophenylhydrazones of the epoxyketones and the bis-2, 4-dinitrophenylhydrazones of the α-diketones, after recrystallization from alcohol or alcohol + ethyl acetate formed very small orange or dark red crystals. The dioximes formed colorless needle-shaped crystals (from aqueous alcohol). Table 2 gives analytical data for the compounds prepared.

Table 1

Properties of Epoxyketone and α-Diketones Synthesized

Compound no.	Compound	R	R′	Bp °C (pressure, mm)	d_4^{20}	n_D^{20}	MR_D Found	MR_D Calculated	Yield, %
I	2,3-Epoxyheptanone-4	C_3H_7	CH_3	44—45 (3)	0.9472	1.4322	35.07	34.69	53
II	3,4-Epoxyoctanone-5	C_3H_7	C_2H_5	48 (2)	0.9248	1.4320	39.80	39.31	52
III	4,5-Epoxynonanone-6	C_3H_7	C_3H_7	72 (3)	0.9344	1.4335	43.54	43.93	46
IV	2-Methyl-5,6-epoxyheptanone-4	i-C_4H_9	CH_3	59—61 (6)	0.9340	1.4280	39.11	39.30	56
V	2-Methyl-5,6-epoxyoctanone-4	i-C_4H_9	C_2H_5	70—71 (5)	0.9148	1.4302	44.04	43.92	71
VI	2-Methyl-5,6-epoxynonanone-4	i-C_4H_9	C_3H_7	77—79 (4)	0.9071	1.4360	48.98	48.53	55
VII	Heptondione-3,4	C_3H_7	CH_3	146—148 (750)*	—	—	—	—	56
VIII	Octandione-4,5	C_3H_7	C_2H_5	165—168 (750)**	—	—	—	—	78
IX	Nonandione-4,5	C_3H_7	C_3H_7	97—99 (28)***	—	—	—	—	60
X	2-Methylheptandione-4,5	i-C_4H_9	CH_3	170—173 (750)	0.9019	1.4318	40.66	39.17	63
XI	2-Methyloctandione-4,5	i-C_4H_9	C_2H_5	180—183 (752)	0.927	1.4380	44.2	43.78	72
XII	2-Methylnonandione-4,5	i-C_4H_9	C_3H_7	103—105 (23)	0.9056	1.4340	48.91	48.40	57

*In [4] bp 147° (732 mm)
**In [5] bp 168°; 60° (12 mm)
***In [6] bp 75.5° (15 mm)

Table 2

Analytical Data for Compounds Synthesized

Compound no.	Formula	M		Found, %		Calculated, %		2,4-Dinitrophenylhydrazones			Dioximes, mp, °C
		Found, %	Calculated, %	C	H	C	H	Mp, °C	N, % Found, %	N, % Calculated, %	
I	$C_7H_{12}O_2$	129 128.5	128	66.18 66.12	9.64 9.70	65.62	9.37	119—120	17.47 17.61	18.12	—
II	$C_8H_{14}O_2$	138 136.6	142	68.16 67.94	9.81 9.84	67.61	9.87	123—124	16.91 16.80	17.36	—
III	$C_9H_{16}O_2$	154 150	156	69.70 69.47	10.34 10.60	69.23	10.25	91—92	16.95 16.90	16.66	—
IV	$C_8H_{14}O_2$	143 139	142	66.90 67.31	9.71 9.85	67.61	9.87	186—188	16.92 17.80	17.36	—
V	$C_9H_{16}O_2$	161 158	156	68.89 68.93	10.69 10.60	69.23	10.25	192—193	17.03 16.36	16.66	—
VI	$C_{10}H_{18}O_2$	177 165	170	70.75 71.00	10.80 10.91	70.59	10.59	156	16.57 16.11	16.00	—
VII	$C_7H_{12}O_2$	—	—	—	—	—	—	—	—	—	168*
VIII	$C_8H_{14}O_2$	—	—	—	—	—	—	—	—	—	185—186**
IX	$C_9H_{16}O_2$	—	—	—	—	—	—	—	—	—	170—171***
X	$C_8H_{14}O_2$	—	—	67.06 67.13	10.27 10.34	67.61	9.87	—	—	—	—
XI	$C_9H_{16}O_2$	—	—	69.39 69.29	10.52 10.60	69.23	10.25	196	21.68 21.93	21.64	—
XII	$C_{10}H_{18}O_2$	—	—	70.25 70.28	10.92 10.89	70.59	10.59	190—192	21.16 21.26	21.13	—

* In [4] mp 167-168°.

** In [5] mp 186-187°.

*** In [6] mp 172°.

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