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Oxidation of 1-Cyclohex-1-enecarbaldehyde and Related Compounds with Caro's Acid

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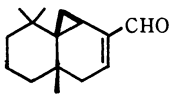
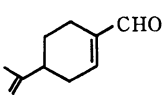
Synopsis. Three cyclic α,β-unsaturated aldehydes (**1**—**3**) were oxidized with an equivalent of Caro's acid in methanol, giving both simple oxidation products and the corresponding norketones in moderate yields.

The Baeyer-Villiger oxidation of α,β-unsaturated ketones has been investigated extensively with various acids.[1] However, only a few reports were given on the reactions of α,β-unsaturated aldehydes[2] with Caro's acid. In connection with the chemical reactivity of thujopsene,[3] we have examined the oxidations of a few cyclic, α,β-unsaturated aldehydes. The results are given in this paper.

Three aldehydes, (−)-*cis*-thujopsenal (**1**), (−)-perillaldehyde (**2**) and 1-cyclohex-1-enecarbaldehyde (**3**), were used as starting materials. Oxidation was carried out in methanol with an equivalent of Caro's acid. The products were separated and purified by gas, thin layer and column chromatography and identified by spectral data (see Experimental). The results are summarized in Table 1.



1



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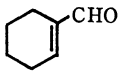


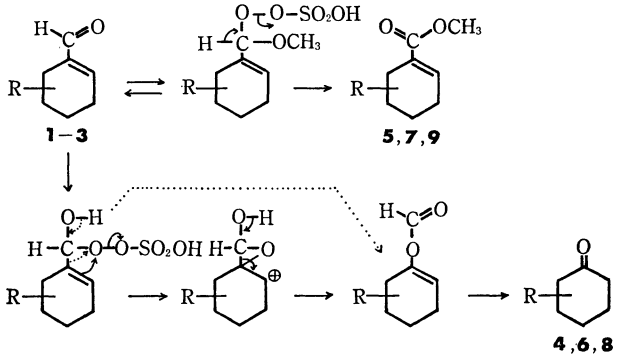
3

Methyl esters (**5**, **7** and **9**), formed by simple oxidation, and the corresponding norketones (**4**, **6** and **8**) were formed with moderate yields, the ratios apparently depending on the steric structures of starting aldehydes. The norketones might be produced *via* cyclohexenyl formates as depicted in the Scheme. In general, the major products of the Baeyer-Villiger oxidation of α,β-unsaturated ketones are the epoxy esters, which are no doubt derived from the enol esters.[1a] Norketones might be formed by the facile methanolysis of enol formates.

Table 1. Oxidation of cyclic α,β-unsaturated aldehydes with Caro's acid

Aldehydes	Conversion[a]	Products and yields (%)[b]	
		Methyl esters	Norketones
1	97.2	**5** 10.2 (6.7)	**4** 55.4(39.0)
2	100.0	**7** 42.0(25.0)	**6** 26.5(20.7)
3	88.8	**9** 10.2 (6.3)	**8** 33.5(29.6)

a) Figures denote 100×(moles of aldehydes reacted/moles of aldehydes charged). b) Calculated by glc. Figures in parentheses give yields of isolated products.



1—3 **5,7,9** **4,6,8**

Experimental

Melting points were determined with a Büchi melting-point apparatus and are uncorrected. The homogenity of each compound was confirmed by tlc over silica gel (Merck G) and/or by glc (Shimadzu GC-1C) over 15% Silicon OV-17 Uniport (column A) and diethylene glycol succinate on Shimalite (B), using naphthalene as an internal standard. The UV and IR spectra were measured in ethanol and CCl_4, respectively. The NMR spectra were obtained in CCl_4, at 60 and/or 100 MHz, unless otherwise stated, TMS being used as an internal reference. Abbreviations "s" and "m" denote singlet and multiplet, respectively.

Oxidation of (−)-cis-Thujopsenal (1). To a solution of **1**[3] (4.4 g), mp 74—75 °C, prepared by SeO_2 oxidation[4] of thujopsene, in anhydrous methanol kept at 10 °C was added dropwise Caro's acid (10.4 g), prepared from ammonium persulfate (4.6 g) and 85% sulfuric acid (5.8 g), for 30 min. The solution was stirred at 15 °C for 4 hr, then poured into ice-water and extracted with ether. The ether solution was washed with water, dried over anhydrous Na_2SO_4 and evaporated to leave a crude product (4.1 g), which crystallized partially and was found to contain 6 components by glc (column A, 180 °C). The crystalline material was collected by filtration and then recrystallized from ethyl acetate to give pure colorless crystals (1.6 g), mp 108—109 °C, identified as thujopsene anhydrodihydroketone[5] (**4**) by direct comparison with the authentic specimen; Mass, *m/e* 206 (M^+); UV, λ_{max} 207 nm (ε 5500); IR, ν_{max} 3020, 1690 and 1679 cm^{-1}; NMR ($CDCl_3$), δ 0.59, 1.10 and 1.17 (each 3H, s, CH_3) Found: C, 81.34; H, 10.49%; mol wt (Rast, benzene), 205. Calcd for $C_{14}H_{22}O$: C, 81.55; H, 10.68%; mol wt, 206.3.

The mother liquors obtained by filtration and recrystallization were evaporated and purified by preparative tlc with 3 : 97 mixture of ethyl acetate and *n*-hexane to give colorless crystals (0.33 g), mp 105—106 °C, identified as methyl thujopsenate[6] (**5**); IR, ν_{max} 3010, 1718, 1713, 1652, and 1086 cm^{-1}; NMR, δ 0.72 1,11 and 1.17 (each 3H, s, CH_3), 3.65

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(3H, s, $COOCH_3$), and 6.41 (1H, m, olefinic H). Found: C, 77.25; H, 9.59%; mol wt (Rast), 246. Calcd for $C_{16}H_{24}O_2$: C, 77.38; H, 9.74; mol wt, 248.4.

*Oxidation of (−)-Perillaldehyde (**2**).* Aldehyde **2** (3.0 g), bp 92.5—93.5 °C/5 mmHg (Nippon Terpene Co. Ltd.) purified by treatment with $NaHSO_3$ was oxidized in methanol (24 g) with Caro's acid (10.4 g) in the same manner as **1** afforded an oily product (2.7 g), consisting of 4 components (glc, column B, 145 °C). The product was separated by preparative tlc using a 1 : 9 mixture of ethyl acetate and *m*-hexane to give two compounds, colorless (0.57 g) and pale yellow oil (0.9 g), in pure state. The former was identified as 4-isopropenylcyclohexanone[7] (**6**); UV, λ_{max} 205 nm (ε 1000); IR, ν_{max} 1717, 1645 and 892 cm^{-1}; NMR, δ 1.73 (3H, s, CH_3) and 4.80 (2H, s, exo CH_2). Found: C, 78.10; H, 10.15%. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21%.

The latter was identified as methyl 1-(4-isopropenylcyclohex-1-ene)carboxylate[8] (**7**); IR, ν_{max} 1712, 1646, 1245, and 887 cm^{-1}; NMR, δ 1.70 (3H, s, CH_3), 3.64 (3H, s, $COOCH_3$), 4.72 (2H, s, exo CH_2), and 6.82 (1H, m, olefinic H). Found: C, 73.20; H, 8.82%; mol wt (Rast), 179. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95%; mol wt, 180.3.

*Oxidation of 1-Cyclohex-1-enecarbaldehyde (**3**).* The oxidation of **3**[3] (3.3 g), bp 67—68 °C/13 mmHg, in methanol (25 g) was carried out with Caro's acid (15.6 g) in the same way as for **1** and an oily product (2.6 g). The product was found to consist of 6 components by glc (column A, 165 °C), from which two compounds, cyclohexanone (**8**) (0.88 g) methyl 1-cyclohex-1-enecarboxylate[9] (**9**) (0.26 g), were isolated in pure state by preparative glc with a 2 m × 10 mm column of 20% Silicone SE-30 on Chromosorb W. Ester (**9**) gave the following data; IR, ν_{max} 1718, 1712, 1648, and 1083 cm^{-1}; NMR, δ 3.59 (3H, s, $COOCH_3$) and 6.82 (1H, m, olefinic H). Found: C, 68.35; H, 8.48%. Calcd for $C_8H_{12}O_2$: C, 68.55; H, 8.63%.

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