## Preparation of a-Nitro Olefins from a-Halo Ketoximes

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(Received July 23, 1981)

Synopsis.  $\alpha$ -Nitro olefins were synthesized from  $\alpha$ -haloketones through oximation and subsequent oxidation with trifluoroperacetic acid.

 $\alpha$ -Nitro olefins are versatile and unique synthetic intermediates, for examples, for the introduction of nucleophiles and electrophiles at the  $\beta$ - and  $\alpha$ -carbon atom, respectively, or for annulation reactions.<sup>1,2)</sup> Furthermore the nitro group is convertible into such a function as an amino or a carbonyl group.<sup>1)</sup>

Although the conversion of  $\alpha$ -nitro olefins into the  $\alpha$ -chloro ketoximes was reported,<sup>3)</sup> the reverse reaction is not developed. This reaction seems to be attractive because  $\alpha$ -chloro ketoximes are prepared in good yields by the reaction of olefins with nitrosyl chloride in the presence of hydrochloric acid.<sup>4)</sup>

In this paper we described the preparation of  $\alpha$ -nitro olefins from  $\alpha$ -halo ketones according to Eq. 1, in which the nitro group could be introduced regionselectively.

Although the ketoximes were generally prepared by

$$2e + 1e \rightarrow \bigcirc \stackrel{HON}{\longrightarrow} \stackrel{HON}{\longrightarrow} \stackrel{Me}{\longrightarrow} OMe$$

treatment of the ketones with hydroxylamine acetate or hydroxylamine hydrochloride in the presence of such a weak base as sodium acetate, oximation of 2-chlorocyclohexanone by the conventional methods afforded a complex mixture. However, the desired 2-chlorocyclohexanone oxime was obtained in 64% yield with 2-chloro-1,1-dimethoxycyclohexane together (17.5%) by treatment with hydroxylamine hydrochloride in methanol.<sup>5)</sup> Similar treatment of several α-halo ketones provided the corresponding α-halo ketoximes in moderate yields (Table 1). Under the same conditions, however, 2-chloro-2-methylcyclohexanone did not afford the expected oxime, but 2-methyl-2cyclohexenone oxime (4) (39% yield) and 2-methoxy-2methylcyclohexanone oxime (5) (23% yield).

The oximes 2 were oxidized with trifluoroperacetic acid in acetonitrile in the presence of disodium hydrogenphosphate and urea,  $^{6}$ ) giving the corresponding  $\alpha$ -nitro olefin in moderate yield as shown in Table 1.

Similar oxidation of 5 yielded 2-methyl-1-nitrocyclohexene in 40% yield.

## **Experimental**

IR spectra were recorded with a Hitachi 285 Infrared Spectrophotometer. NMR spectra were determined with a Varian EM 360A NMR Spectrometer. GLC analyses were performed with a Varian 940 instrument equipped with an OV 101 column (N,N-diethylaniline as internal standard). Column chromatography was carried out on silica gel (C-300, Wakogel).

2-Chlorocyclohexanone Oxime. Typical Procedure: To a solution of 2-chlorocyclohexanone (1.325 g, 10 mmol) in methanol (6 mL) was added hydroxylamine hydrochloride (765 mg, 11 mmol). The mixture was stirred at room temperature for 2 h and then worked up in the usual way to give a syrup. The syrup was chromatographed on silica gel, eluting with benzene-ethyl acetate (25:1, v/v) to afford 944 mg (64%) of the oxime and 312 mg of 2-chloro-1,1-dimethoxycyclohexane (17.5%). Without further purification the oxime was used for oxidation.

1-Nitrocyclohexene. Typical Procedure: An acetonitrile solution (90 mL) of 2-chlorocyclohexanone oxime (590 mg, 4 mmol) was added dropwise a stirred solution of oxidant, prepared by mixing successively acetonitrile (10 mL), trifluoroacetic anhydride (2.0 mL), 90% aqueous hydrogen peroxide

Table 1. Conversion of  $\alpha$ -haloketones (1) into  $\alpha$ -nitro olefins (3) and spectroscopic data of 3

α-Halo ketone	Oxime	Yield/%	α-Nitro olefin	Yield/% a)	IR (NaCl) NO <sub>2</sub> ( $\tilde{\nu}/\mathrm{cm}^{-1}$ )	<sup>1</sup> H NMR (CDCl <sub>3</sub> ) Olefinic proton(s) (δ)
la	2a	61	3a	31 (43)	1515, 1335	7.25 (1H, q)
1 <b>b</b>	2b	63	3ь	66	1520, 1335	6.36 (1H, d), 5.49 (1H, s <sup>b</sup> )
1c	2c	64	3c	42 (68)	1510, 1335	7.34 (1H, q)
1d	2 <b>d</b>	58	3d	45 (74)	1510, 1335	7.34 (1H, q)
1e	5	23	3е	40 (62)	1505, 1320	
1f	<b>2f</b>	59	3f	38 (61)	1505, 1355	7.00 (1H, m)

a) Isolated yield from 2; figures in parentheses show the yields based on GLC analyses. b) Broad singlet.

(0.35 mL), disodium hydrogenphosphate (5.2 g), and urea (0.08 g). After the mixture had been stirred for 30 min at ambient temperature, cold water (20 mL) was added gradually. The solution was extracted with diethyl ether  $(20 \text{ mL} \times 3)$ , and the extracts were successively washed with saturated aqueous solution of sodium hydrogencarbonate and of sodium chloride, dried over MgSO<sub>4</sub>, and evaporated. The residue was chromatographed on silica gel, eluting with benzenecyclohexane (1:2, v/v) to give 213.4 mg (42%) of 1-nitrocyclohexene, identical with an authentic sample by IR and NMR spectroscopy.

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