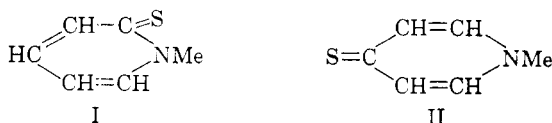


been established^{1,2} that the frequency of the unperturbed thiocarbonyl stretching vibration is $1140 \pm 80 \text{ cm.}^{-1}$ (in agreement with semiempirical calculation³). This frequency is rather insensitive to polar effects, but accidental resonance,^{4,5} e.g. with the NH_2 wagging vibration ($\sim 1130 \text{ cm.}^{-1}$) in $-\text{CS}\cdot\text{NH}_2$ derivatives, or with asymmetric N-C-N stretching ($1100\text{--}1200 \text{ cm.}^{-1}$) in $-\text{N}\cdot\text{CS}\cdot\text{N}-$ derivatives, may give rise to absorption bands in different positions due to "mixed" vibrations.

The applicability of infrared spectroscopy to studies of thiol-thione equilibria such as are at present being pursued in this Department⁶ was examined, and conjugated C=S groups have been found to give rise to absorption bands as intense as carbonyl stretching bands. The infrared spectra of I and II have been compared with those of the corresponding carbonyl compounds (O in place of S). Strong absorption in the range $1110\text{--}1145 \text{ cm.}^{-1}$ is observed in the spectra of the thio-compounds, while the oxo-compounds display only comparatively weak absorption in this region ($\epsilon \leq 60$). No other band characteristic of the C=S group, and absent from the spectra of the C=O derivatives, has been found. The maximal intensity observed for II is among the highest recorded for infrared absorption bands.

TABLE I



FREQUENCIES (ν in cm.^{-1}) AND APPARENT^a INTENSITIES (ϵ_{max} IN l. cm. mole^{-1}) OF THIOCARBONYL STRETCHING BANDS IN THE INFRARED^b

Compound	State	ν	ϵ_{max}
I	Soln. in CS_2	1114, 1142	475, 250
I	Soln. in CCl_4	1117, 1143	470, 280
II	Soln. in CS_2	1127	1450
II	Solid in KBr	1111	
I, H in place of Me	Soln. in CS_2	1144	525
I, H in place of Me	Soln. in CHCl_3	1143	(strong)
II, H in place of Me	Soln. in CHCl_3	1126	(strong)
II, H in place of Me	Solid in KBr	1111, 1122	

^a Not corrected for finite slit widths. ^b Measured on a single-beam single-pass spectrometer.

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2- and 4-Mercaptopyridine in aqueous solution have been shown to be principally thiones,⁶ i.e. I and II with H in place of Me, in analogy with 2- and 4-hydroxypyridine which actually are predominantly carbonyl compounds.^{7,8} The data in the table show that these mercaptopyridines are essentially thiocarbonyl compounds also in less polar media. This study is being extended.³

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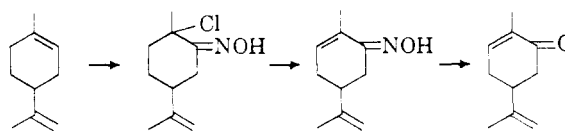
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Nitrosochloride Syntheses and Preparation of Carvone

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A convenient preparation of limonene nitrosochloride has been developed. In place of the usual generation of nitrosyl chloride in a separate generator or the use of amyl nitrate it has been found that nitrosochlorides can be formed *in situ* by simultaneous addition of sodium nitrite and acid to the olefin. Yields by the procedure are high, and the quality of the product is satisfactory. Limonene nitrosochloride can be produced in yields of 80% with rotations of 226° .



The amount of acid used in the reaction is critical. The usual amount of concentrated aqueous hydrochloric acid used was 40–50 ml. per tenth mole of olefin. As low as 33.3 ml. per tenth mole of olefin gave nearly the same results. Use of 75 ml. of concentrated acid per tenth mole of olefin reduced the yield from the usual 75–80% range to less than 10%. In general, equimolar proportions of sodium nitrite were used although a 50% excess had no adverse effects. The temperature of the reaction had to be maintained below 10° . Operation at 20° resulted in a 26% yield of nitrosochloride. The rate of addition and the efficiency of stirring had to be adjusted to avoid localized heating and high acid concentrations even with optimum amounts of reagents.

Other cyclohexene derivatives can be converted to the nitrosochlorides by the same process. Using the conditions found optimum for limonene, yields

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of nitrosochlorides from cyclohexene, 1-menthene, and α -pinene were 8.3%, 20.1%, and 6.8% respectively. Optimum conditions were not sought, although it is known that with limonene, when reaction conditions were less than optimum, the yield of nitrosochloride fell off immediately to these lower levels.

Limonene nitrosochloride is relatively stable when purified by repeated washings with cold isopropyl alcohol. Some separation of forms of the derivative are observed and the less soluble material obtained upon excessive washing, in 63% yield, had a rotation of 340° . The nitrosochloride undergoes decomposition upon standing. A brown oil is formed and this then crystallizes after several days standing at room temperature. The latter material is carvoxime. The progress of the decomposition can be followed by the loss in weight as well as by the change from positive to negative rotation. Conversions of the nitrosochloride to carvoxime described in the literature using pyridine and acetone^{2,3} or urea and isopropyl alcohol³ were found to work well. It was observed, however, that the amounts of reagents specified are excessive and that the reaction occurs under much milder conditions with less decomposition. The progress of the reaction was followed by the change in rotation of the solution. The use of sodium hydroxide or McElvain's buffer⁴ was not useful. The use of dimethylformamide was found to work at least as well as pyridine or urea.

A significant improvement in the quality of the carvone produced by decomposition of carvoxime was obtained when the reaction was run on a continuous basis. The control of pH as suggested³ was found to be desirable. In order to minimize the time of contact of the carboxime and carvone with the acidic media, carvoxime was added as a melt or as a slurry in water during the reaction. Carvone was steam distilled out of the reaction mixture as rapidly as it was formed. A yield of 83% of the theoretical amount of carvone from the oxide was obtained. The product had a rotation of -58.8° , which is significantly higher than from other methods of synthesis.

EXPERIMENTAL

Limonene nitrosochloride. A solution of 40.8 g. (0.3 mole) of (+)-limonene ($\alpha_D +95^\circ$) in 40 ml. of isopropyl alcohol was cooled below 10° . To this were added simultaneously through separate dropping funnels a solution of 120 ml. of concentrated hydrochloric acid in 80 ml. of isopropyl alcohol and a concentrated aqueous solution of 20.7 g. (0.3 mole) sodium nitrite. The addition was adjusted so as to maintain the temperature below 10° . The mixture was stirred for an additional 15 min. and was allowed to stand in the refriger-

ator for 1 hr. The solid, isolated by filtration, was washed with enough cold ethanol to make a thick slurry to provide a water white product. A small amount of additional solid could be isolated from the mother liquors from the washing by cooling and filtration. A total of 161.4 g. (80.7% of theory) of product with a rotation in ethanol of 226° was obtained.

Carvoxime. Eight grams of limonene nitrosochloride and 4 ml. of dimethylformamide were boiled 30 min. under reflux in 25 ml. of isopropyl alcohol. The product at the end of this time had a constant negative rotation. It was poured into 150 ml. of cracked ice and water, stirred vigorously, and was filtered after the ice was melted. The solid was washed three times with 10 ml. of cold water and once with 3 ml. of cold isopropyl alcohol. The dry product weighed 5.47 g. (83.5%) m.p. $66-69^\circ$, $\alpha_D -40.3^\circ$, and was pure enough for further work.

Carvone. A one liter three-necked flask was fitted with a Beckman high temperature glass electrode 8890-15, a reference electrode 8970-92, and outlets which allowed addition of sulfuric acid, addition of oxime, and distillation of water-product azeotrope. In the flask was placed 700 ml. of water which was brought to boiling, and the pH was adjusted to 0.8 with 3*N* sulfuric acid. About 50 ml. of acid was required. Then carvoxime was added dropwise from a separatory funnel in which solid oxime was melted in portions by means of an infrared lamp. Evolution of carvone was nearly instantaneous and the addition was so regulated that the carvone in the still pot could be voided within 5 min. About 1.25 hr. were required for the addition. Dilute sulfuric acid was added portionwise during the reaction to maintain the pH at 0.7-0.9. A total of 85 ml. of 3*N* sulfuric acid was used. The product was isolated in a continuous separator and the condensate water returned to the still pot. A total of 18.6 g. (83% yield) of white carvone with a rotation of -58.8° was obtained.

A similar reaction was run in which solid carvoxime was added through a condenser directly to the still pot without prior melting. The yield was 18.8 g. and the rotation again was -58.8° .

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Infrared Spectra of 6,6-Dialkylfulvenes

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Because of the recent increased interest in the infrared spectra of the fulvenes^{1,2} and in view of papers on 6-monosubstituted fulvenes,³ and phenyl-substituted fulvenes,^{4,5} we believe it would be useful to publish the infrared spectra of the 6,6-dialkyl substituted fulvenes.

Table I lists moderately strong and strong bands of these fulvenes, and Fig. 1 is a typical spectrum. The bands reported form a persistent pattern. Differences between the spectra of these fulvenes

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