

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 refrigerator

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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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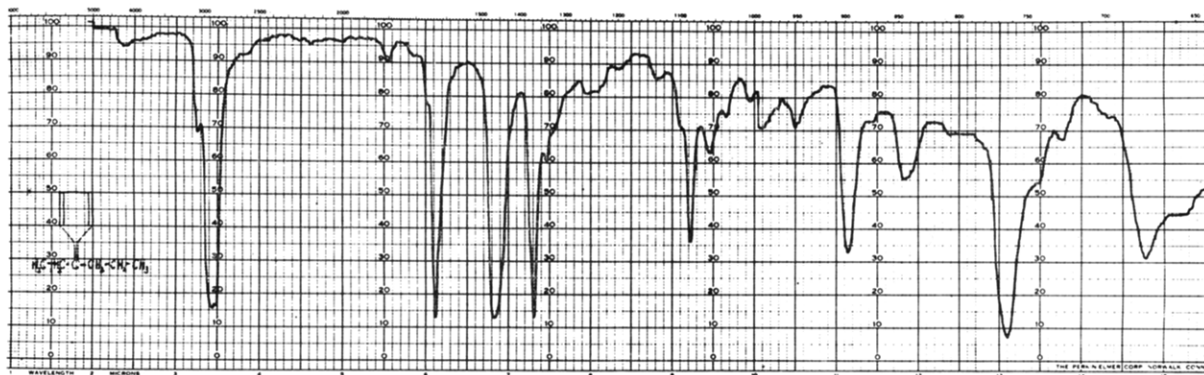


Fig. 1 The infrared spectrum of 6-ethyl-6-*n*-propyl fulvene.

are evident in the weak to medium bands, and in some degree in the differences in relative intensities of the strong bands. Any major differences in the number or position of strong bands reflect major differences in the kind of substituents on the fulvene moiety.

TABLE I^a

PRINCIPAL INFRARED BANDS OF 6,6-DIALKYLFULVENES	
Cm. ⁻¹	Description
2950-2900	Strong, sharp band, with typical sharp shoulder band at 3030-3080. Dimethylfulvene has additional notable inflections at 2980 and 2880
1820-1785	This is a weak band centering at 1800, probably a C=C-H bending overtone. It is noted here because it is persistent and in an otherwise transparent region
1647-1640	Strong to very strong, sharp, characteristic probably of the fulvene exocyclic double bond. It lies at 1629 for 6-furyl-(2)-fulvenes, and Thiec and Wiemann give 1632 for dimethylfulvene, which we find at 1642. For heavily substituted fulvenes it may be as low as 1597 (ref. 5)
1475-1465 and 1443-1437	This pair is medium to strong; their relative intensities depend on the substituents. They are about equal in dimethylfulvene, 1470 being slightly stronger; about equal in ethylmethylfulvene but 1440 is stronger; in methyl- <i>n</i> -heptylfulvene 1440 is a shoulder; in ethyl- <i>n</i> -propylfulvene 1440 is an inflection. The 1475-1465 band is accompanied by a band of inflection to medium strength at 1458-1440
1375-1368	Very strong, sharp
1090-1085	Medium to strong, sharp
920-878	Weak to strong
764-752	Very strong, wider than the others but centering in the region given
728-724	Weak to very strong
705-700	Inflection to medium band
677-674	Weak to strong

^a This table reports the moderately strong to strong bands in 6,6-dialkylfulvenes, based on the spectra of dimethyl, ethylmethyl, diethyl, methyl-*n*-propyl, methylisopropyl, methyl-*n*-pentyl, ethyl-*n*-propyl, and methyl-*n*-heptylfulvenes.

It should be noted that the spectra bear a resemblance to that of dicyclopentadiene, except that relative intensities of bands are quite different. Both dicyclopentadiene and cyclopentadiene are possible impurities, hence we have found certain bands particularly useful for checking for their presence; dicyclopentadiene has two strong bands, at 807 and 821 cm.⁻¹, which is a relatively transparent part of the fulvene spectrum; and cyclopentadiene has a strong band at 3120 cm.⁻¹ which is absent from the fulvene spectrum.

Since the liquid fulvenes can take up oxygen from the air, we ran spectra on several samples which had had air bubbled through them for several hours. The oxygenated fulvenes show a new band at about 3400 cm.⁻¹ and another at about 1600 cm.⁻¹, with a broad region of absorption from 1050 to 1000 cm.⁻¹, with loss of the typical fulvene band at 1642 cm.⁻¹

EXPERIMENTAL

The fulvenes were prepared by the usual basic condensation of ketone and cyclopentadiene⁶ but with a variety of purification methods, including vacuum distillation and chromatography. Most of the spectra were run several times and in a variety of ways; in about 10% concentration in CCl₄, in CS₂, and as pure liquid in 0.10-mm. and 0.025-mm. cells, and on two different machines, a Perkin-Elmer 21 and a Beckmann IR-4. Some differences in spectra were noted due to dilutions. Most of the samples were prepared independently by both of the two authors. All spectra were run on freshly prepared samples.

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