[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

The Structure of Styrene Oxide Dimers. I. Ultraviolet Spectra of 2,5-Diphenyl-1,4-dioxanes and Related Compounds

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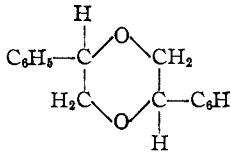
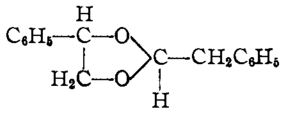
Ultraviolet spectra of a number of aryl-substituted dioxanes and related compounds are reported. The number of apparent maxima in diaryldioxanes increases as the phenyl groups approach each other in space. Thus, in *trans*-2,5-diphenyl-1,4-dioxane, only one maximum is clearly visible, in the *cis* structure, two, and in 2,3-diphenyl-1,4-dioxane a third absorption band appears. The ratio ϵ_1/ϵ_2[2] of the two characteristic maxima appears to be constant for compounds which are very closely related structurally.

Introduction

Chemical evidence[3] has been presented for the structures of styrene oxide dimers, obtained by catalytic dimerization of the monomer with strong acids. It was also shown that the two isomeric compounds obtained from the reaction of phenylmagnesium bromide with 2,5-dichloro-1,4-dioxane were *cis*- and *trans*-2,5-diphenyl-1,4-dioxanes,[4] identical with isomers (I) from the styrene oxide dimerization. The present communication presents the ultraviolet spectra of these compounds, together with a suggested correlation of these spectra with those of structurally related compounds.



I



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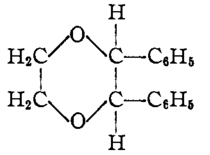

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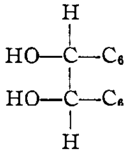
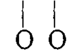


IV

Results and Discussion

Compounds containing phenyl or substituted phenyl groups absorb in the ultraviolet region of the electromagnetic spectrum. A comparison of the spectra of benzene and toluene[5] shows two important effects of the side chain on the ultraviolet absorption of benzene; first, the absorption is shifted toward the red ("hyperconjugation"),[6] and secondly, some of the fine structure exhibited by benzene in the region between 240 and 260 mμ disappears.

Our diaryl-1,4-dioxanes show the expected shifts to longer wave length and relationships between maxima (Fig. 1, curve 3; Figs. 3, 4 and 5). In addition, the spectra of the isomeric dioxanes indicate a possible correlation between positions of the phenyl groups on the dioxane nucleus and their ultraviolet spectra. Although such a differentiation of the positions of chromophoric groups on saturated systems has not been considered feasible,[7] an examination of compounds (1) through (8) in Table I, all of which contain the grouping



$C_6H_5\text{–}\underset{|}{\overset{}{C}}\text{–}\underset{|}{C}\text{–}$ with O under each C ($C_6H_5\text{–}\underset{O}{C}\text{–}\underset{O}{C}\text{–}$),

reveals a constant ϵ_1/ϵ_2 ratio for the first five substances as well as for the last three. These latter compounds all have their two phenyl groups more favorably situated for mutual steric interaction.

TABLE I

EXTINCTION MAXIMA AND THEIR RATIOS FOR ARYLDIOXANES AND RELATED COMPOUNDS

	Compound	λ_1(max) ϵ_1	λ_2(max) ϵ_2	ϵ_1/ϵ_2
1	Monophenyldioxane	252(infl)	257	0.89
		147	166	
2	*trans*-2,5-Diphenyl-1,4-dioxane	252(infl)	257	.88
		305	346	
3	Phenylethylene glycol	252	258	.90
		162	180	
4	Styrene oxide	254	260	.91
		175	192	
5	2-Benzyl-4-phenyl-1,3-dioxalane	257.5	260	.91
		327	360	
6	*cis*-2,5-Diphenyl-1,4-dioxane	252.5	257.5	.82
		275	336	
7	Hydrobenzoin	253	258	.80
		322	402	
8	2,3-Diphenyl-1,4-dioxane	252	258	.79
		295	372	
9	2,3-Dibenzyl-1,4-dioxane	253.5	259	.86
		334	389	
10	2,3-Di-(*o*-tolyl)-1,4-dioxane	265	272	1.14
		724	634	
11	2,3-Di-(*m*-tolyl)-1,4-dioxane	265	272	1.21
		669	553	
12	2,3-Di-(4-chlorophenyl)-1,4-dioxane	260	265	0.96
		564	588	
13	Benzyl ether	252	257	1.07
		660	617	
14	β-Phenethyl alcohol	253	259	0.82
		149	181	

The similarity in spectra of monophenyl-1,4-dioxane and the high melting 2,5-diphenyl-1,4-dioxane isomer (Fig. 4), supported other evidence[3,4] that this was the *trans* isomer. Since the two phenyl groups are separated by the maximum distance in the *trans* isomer, it would be most likely

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[1] 29 Belleaire Avenue, Lynn, Massachusetts.

[2] Where ε is the molecular extinction coefficient in liters moles^{-1} cm.$^{-1}$.

[3] M. J. Kland, Doctoral Dissertation, Northwestern University (1948).

[4] L. A. Bryan, W. M. Smedley and R. K. Summerbell, THIS JOURNAL, **72**, 2206 (1950).

[5] R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, Curves 7 and 8.

[6] See R. S. Mulliken, *J. Chem. Phys.*, **7**, 339, 353 (1939).

[7] I. M. Klotz, *J. Chem. Ed.*, **22**, 328 (1945).

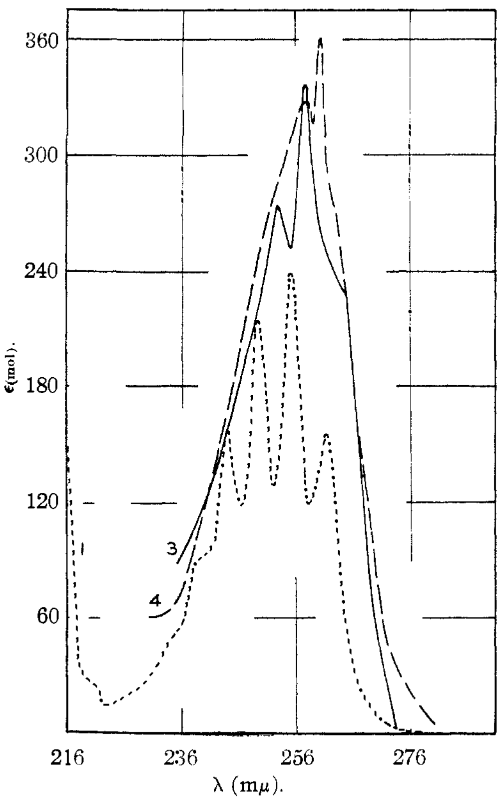


Fig. 1.—1, Benzene; 2, deleted; 3, *cis*-2,5-diphenyl-1,4-dioxane; 4, 2-benzyl-4-phenyl-1,3-dioxolane.

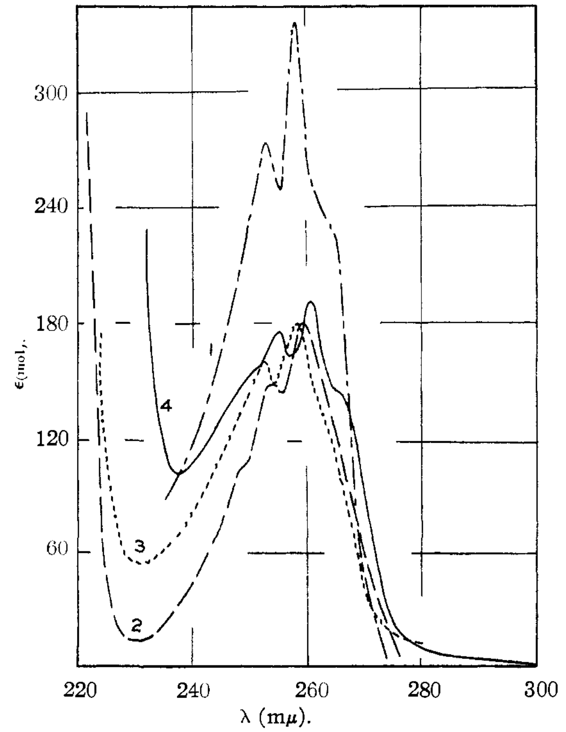


Fig. 2.—1, *cis*-2,5-Diphenyl-1,4-dioxane; 2, β-phenethyl alcohol; 3, phenylethylene glycol; 4, phenylethylene oxide.

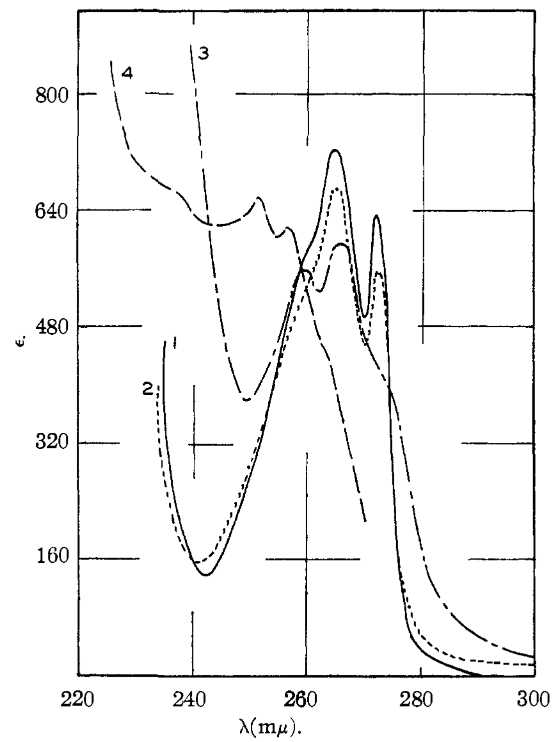


Fig. 3.—1, 2,3-Di-(*o*-tolyl)-1,4-dioxane; 2, 2,3-di-(*m*-tolyl)-1,4-dioxane; 3, 2,3-di-(4-chlorophenyl)-1,4-dioxane; 4, benzyl ether.

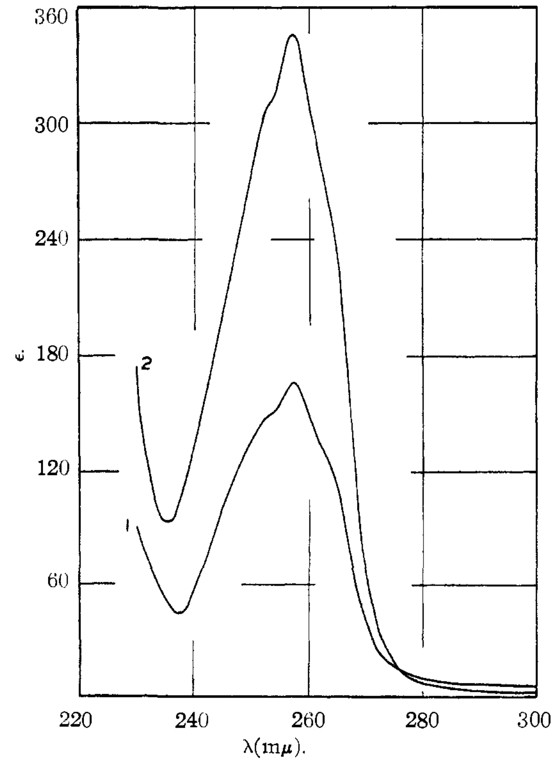


Fig. 4.—1, Monophenyldioxane; 2, *trans*-2,5-diphenyl-1,4-dioxane.

to behave like monophenyldioxane spectrophotometrically. This assigned the *cis* structure to the low-melting isomer (I), a formulation which is consistent with its spectrophotometric relationship to compounds (III) and (IV) indicated in the preceding paragraph.

Although the *cis* and *trans* isomers (I) are both isomeric with the cyclic acetal (II), theb and sepa-

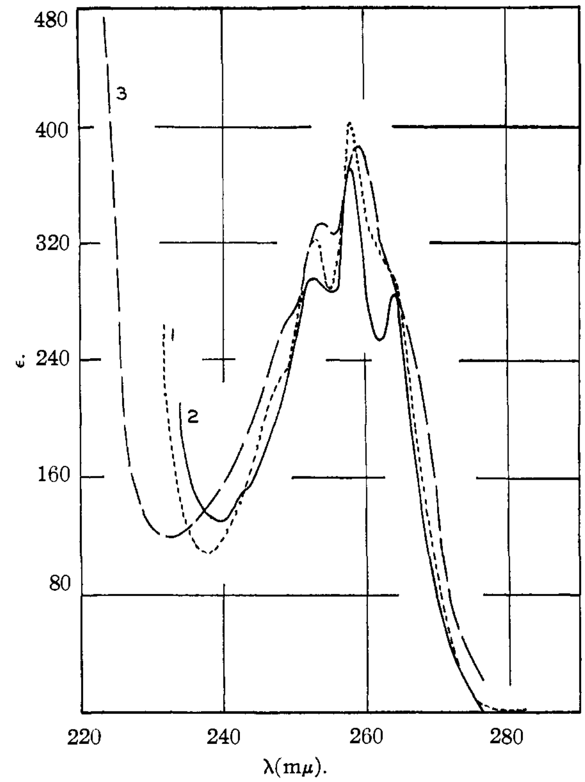
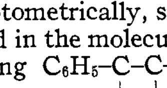


Fig. 5.—1, Hydrobenzoin; 2, 2,3-diphenyl-1,4-dioxane; 3, 2,3-dibenzyl-1,4-dioxane.

ration in the latter compound is appreciably less. It should be noted that in the dioxolane the two phenyl groups are probably not equivalent spectrophotometrically, since they are unsymmetrically located in the molecule, so that consideration of the grouping  $C_6H_5\text{–}\underset{O}{\underset{|}{C}}\text{–}\underset{O}{\underset{|}{C}}\text{–}$ alone in dealing with this spectrum is an oversimplification. The mere fact that the band separation in the dioxolane is approximately half that found for all other compounds listed in Table I raises a question as to the identity of these peaks. Although further analysis along these lines is not at present feasible, the data do present some encouraging evidence that it may be possible to differentiate both structural and stereoisomers of this type, given sufficiently sensitive instrumentation. Such work has already been done by Ramart-Lucas and co-workers,[8,9] but the evidence is as yet inconclusive.

The spectra of 2,3-di-(*o*-tolyl)- and 2,3-di-(*m*-tolyl)-1,4-dioxanes are very similar (Fig. 3), and shifted to slightly longer wave length than toluene itself.

In hydrobenzoin (Fig. 5) as well as the 2,5-diphenyldioxanes, the last benzene band is reduced to a mere inflection point, whereas in 2,3-diphenyl-1,4-dioxane it is clearly apparent. Thus, with the approach of the phenyl groups to one another in the dioxane nucleus, there appears to be an increase in the number of apparent maxima: for example, the

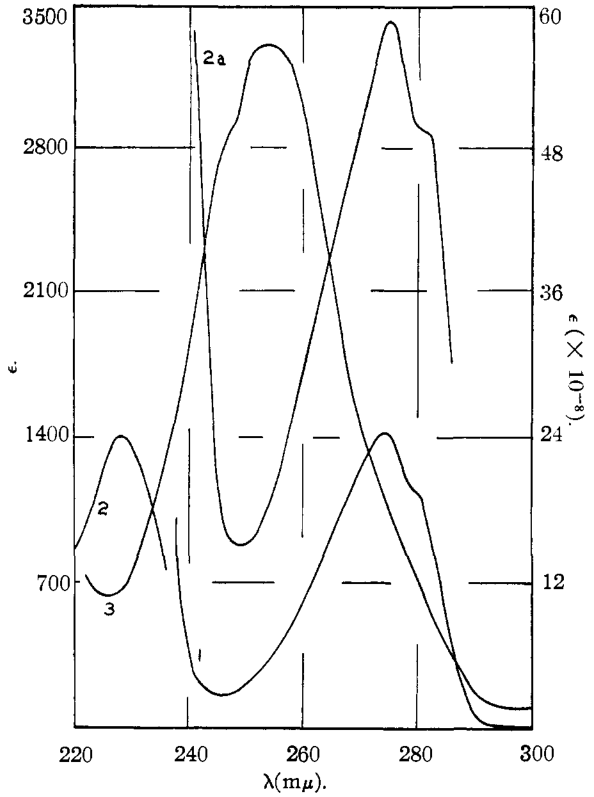


Fig. 6.—1, Mono-*p*-anisyldioxane (ϵ_2); 2, 2,3-di-(4-methoxyphenyl)-1,4-dioxane (ϵ_1); 2a, 2,3-di-(4-methoxyphenyl)-1,4-dioxane (ϵ_2); 3, 2,3-dixenyldioxane, the left hand ordinate is for curves 1 and 2a; the right hand ordinate is for curves 2 and 3.

trans-2,5-diphenyldioxane has only one clearly defined maximum, the *cis* two, and the 2,3-diphenyl analog, three.

The effect of substituting highly unsaturated groups on the benzene ring is illustrated by the spectra of mono-*p*-anisyl-1,4-dioxane, 2,3-di-(4-methoxyphenyl)-1,4-dioxane and 2,3-dixenyl-1,4-dioxane (Fig. 6). Here, any secondary positional influences are masked by first-order resonance effects.

Experimental

All spectra were taken in 95% ethanol, with the solvent as a blank. A Beckman ultraviolet spectrophotometer was used with quartz cells of one cm. length. The spectral region investigated was between 220 and 300 millimicrons. Duplicate readings on an individual sample checked within less than 1%. Concentrations of samples were generally between 10^{-3} and 10^{-4} *M*, and when comparisons between compounds were to be made, the solutions were adjusted, wherever possible, to nearly equal concentrations, to eliminate any colligative factors which might be operative.

1. **Spectra of Commercially Obtained Compounds.**—All liquid substances obtained commercially were redistilled at atmospheric pressure or *in vacuo*, depending on the boiling points, and a middle cut collected for spectrophotometric purposes. The following list of compounds was so treated: benzene, thiophene-free, b.p. 80°; β-phenethyl alcohol (EK 313), b.p. 219°; phenethylene oxide (EK 4789), b.p. 191–192°; benzyl ether (EK 929), b.p. 298°, this compound was purified by refluxing over sodium followed by distillation *in vacuo*.

2. **Substances Synthesized for Investigation.**[3,4]—*cis*-2,5-Diphenyl-1,4-dioxane, m.p. 123°, recrystallized from acetone, alcohol, and/or a mixture of these solvents; *trans*-2,5-diphenyl-1,4-dioxane, m.p. 173–174° (from Grignard synthesis) recrystallized from ether, acetone and chloroform,

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[8] R. Ramart-Lucas and D. Biquard, *Compt. rend.*, **194**, 187 (1932).

[9] R. Ramart-Lucas and F. Salmon-Legagneur, *Bull. soc. chim.*, **51**, 1069 (1932).

m.p. 175° (source, styrene oxide dimerization); recrystallized from ether, acetone, and a mixture of these solvents; 2-benzyl-4-phenyl-1,3-dioxolane, m.p. 41–42°, recrystallized from ethanol and an ether–petroleum ether mixture; phenylethylene glycol, m.p. 66–67°, recrystallized from ether–petroleum ether.

Substances Available from Previous Work at These Laboratories.[10]—All compounds listed were recrystallized from an ether–petroleum ether mixture unless otherwise specified: monophenyl-1,4-dioxane, m.p. 46°, recrystallized from alcohol; 2,3-diphenyl-1,4-dioxane, m.p. 49–50°, recrystallized from petroleum ether; 2,3-dibenzyl-1,4-dioxane, m.p. 62°; 2,3-di-(*o*-tolyl)-1,4-dioxane, m.p. 105–106°; 2,3-di-(*m*-tolyl)-1,4-dioxane, m.p. 84°; 2,3-di-(4-chlorophenyl)-1,4-dioxane, m.p. 152–153°; 2,3-dixenyl-1,4-dioxane, m.p. 145–147°; mono-*p*-anisyl-1,4-dioxane, m.p. 64–66°; 2,3-di-(4-methoxyphenyl)-1,4-dioxane, m.p. 79–80°.

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[10] Summerbell and Bauer, THIS JOURNAL, **57**, 2364 (1935).

[CONTRIBUTION FROM THE DEFENSE RESEARCH LABORATORY, THE UNIVERSITY OF TEXAS]

Allylic Chlorides. XIX.[1] The Hydrochlorination Products of 2,3-Dimethyl-1,3-butadiene[2]

BY LEWIS F. HATCH AND GLEN E. JOURNEAY

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The addition of hydrogen chloride to 2,3-dimethyl-1,3-butadiene yields a mixture of 1-chloro-2,3-dimethyl-2-butene and 3-chloro-2,3-dimethyl-1-butene while hydrochlorination in aqueous medium gives 1,3-dichloro-2,3-dimethylbutane in addition to these monochlorides. These findings are not in agreement with previous literature which characterizes 3-chloro-2,3-dimethyl-1-butene as 1-chloro-2,3-dimethyl-2-butene and lists it as the only product. A study has been made of the reactions of 1-chloro-2,3-dimethyl-2-butene with potassium iodide in acetone and sodium ethoxide in ethanol.

In the course of a study on allylic chlorides it became desirable to prepare 1-chloro-2,3-dimethyl-2-butene and a survey of the literature indicated that several methods for its preparation were available. Tishchenko[3] reported the preparation of this compound by the chlorination of 2,3-dimethyl-2-butene in a manner similar to that used earlier by Chupotsky and Mariutza[4] to prepare an uncharacterized monochloride which was later assumed to have been 1-chloro-2,3-dimethyl-2-butene. In 1947 Howard, *et al.*,[5] reported the addition of hydrogen chloride to 2,3-dimethyl-1,3-butadiene in the presence of zinc chloride to obtain a quantitative yield of 1-chloro-2,3-dimethyl-2-butene. Because of the indicated high yield of the desired compound, the hydrochlorination of 2,3-dimethyl-1,3-butadiene was investigated. The results obtained, however, were not the same as those of Howard and co-workers.

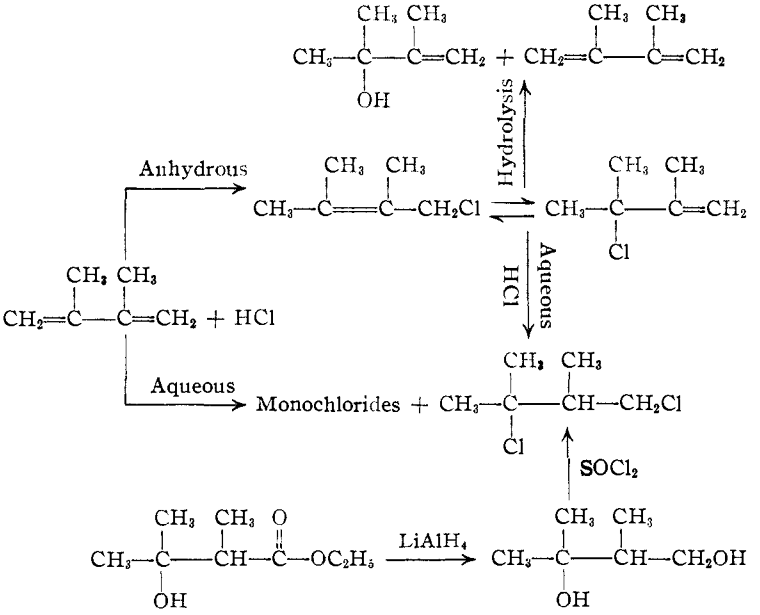

Fig. 1.—Hydrochlorination of 2,3-dimethyl-1,3-butadiene.

It was found that the two synionic isomers, 1-chloro-2,3-dimethyl-2-butene and 3-chloro-2,3-dimethyl-1-butene, were produced by this method of hydrochlorinating 2,3-dimethyl-1,3-butadiene (Fig. 1) and that the relative amounts of the two isomers were dependent upon the temperature at which the reaction took place. Lower reaction temperatures favored the formation of the primary chloride, but the highest yield of this isomer was only 15% at −69°. The monochlorides did not undergo allylic rearrangement under the conditions of the hydrochlorination and no dichloride was produced.

The two monochlorides were characterized by their physical properties and by their infrared spectra. The lower boiling isomer, which is assumed to be the tertiary chloride, has an infrared spectrum containing an absorption at 11.2 μ caused by the $RR'C{=}CH_2$ structure. This band is absent in the higher boiling isomer. The 6.1 μ C=C stretching vibration, present in the spectrum of the lower boiling isomer, could not be detected in the spectrum of the higher boiling compound. It should be very weak in the nearly symmetrical primary chloride and is probably masked by the

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[1] For paper number XVIII of this series, see L. F. Hatch and D. W. McDonald, THIS JOURNAL, **74**, 3328 (1952).

[2] Presented in part at the 121st National Meeting of the American Chemical Society, Buffalo, New York, March, 1951.

[3] D. V. Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*), **8**, 1232 (1938); *C. A.*, **33**, 4130 (1939).

[4] A. Chupotsky and N. Mariutza, *J. Russ. Phys. Chem. Soc.*, **21**, 432 (1889); *Ber.*, **22**, 760 (1889).

[5] F. L. Howard, T. W. Mears, A. Fookson, P. Pomerantz and D. B. Brooks, *J. Research Natl. Bur. Standards*, **38**, 374 (1947).